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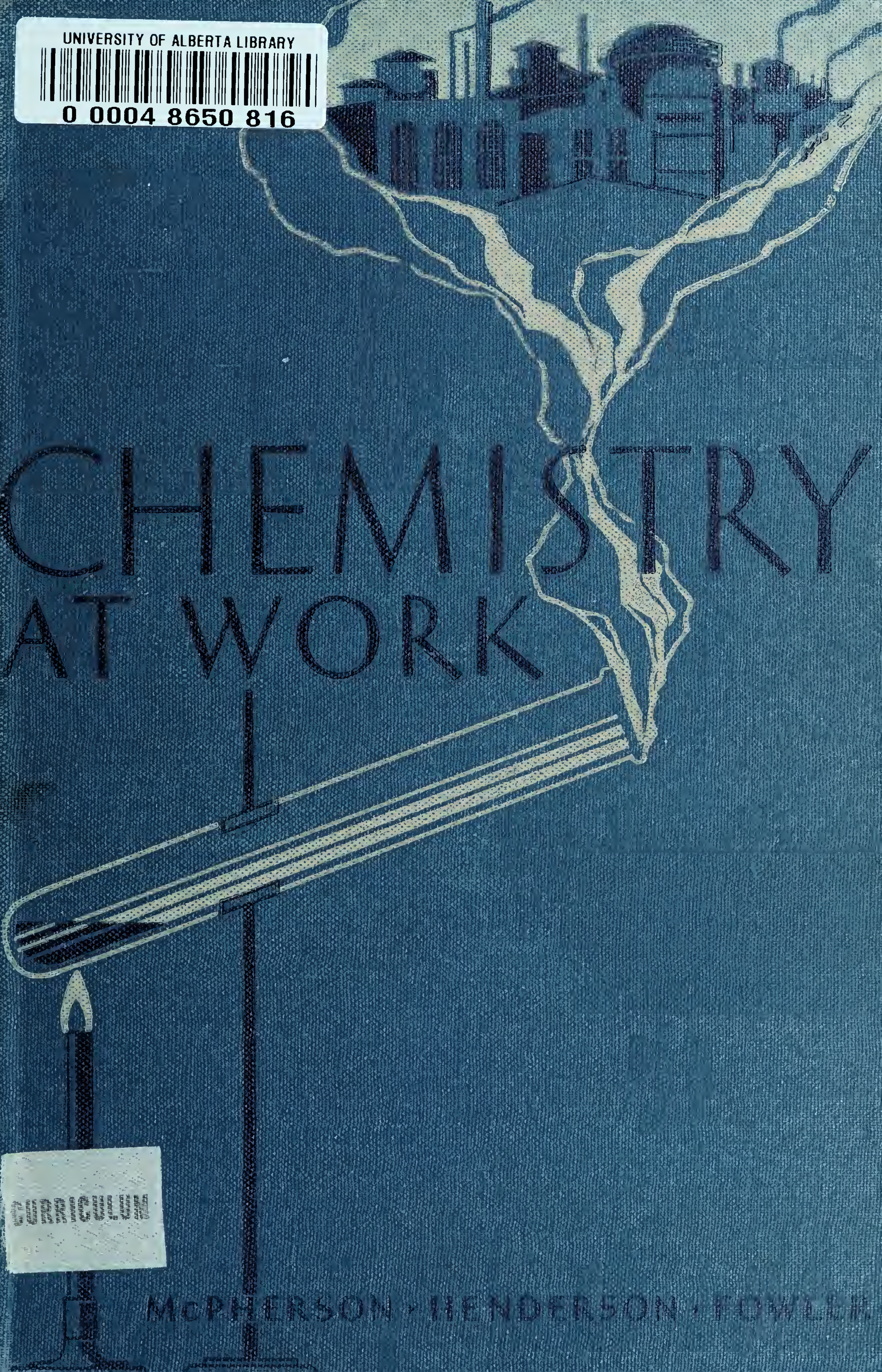

CHEMISTRY AT WORK

McPHERSON · HENDERSON · FOWLER

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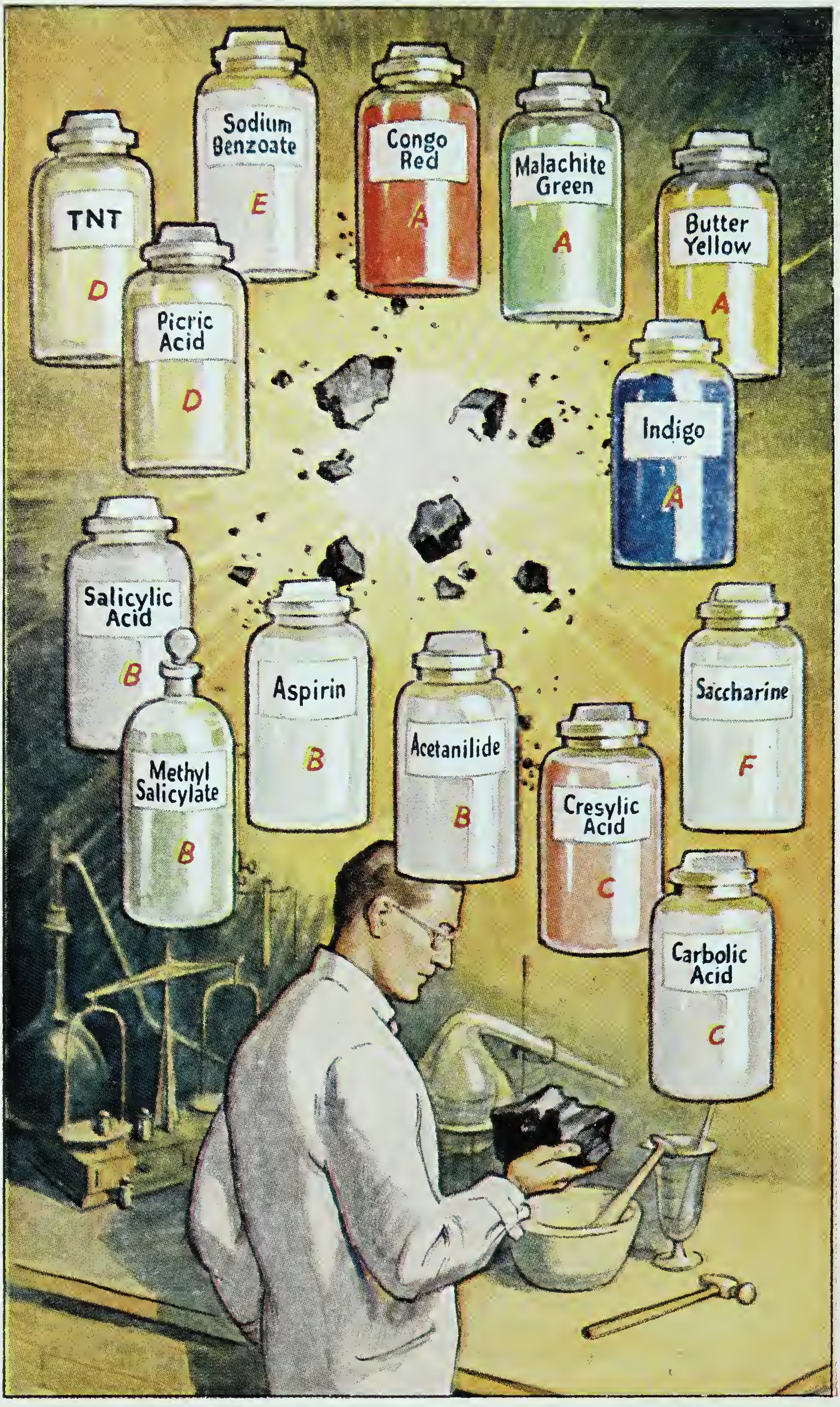
Sodium Benzoate
E
Congo Red
A
Malachite Green
A
TNT
D
Picric Acid
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Butter Yellow
A
Indigo
A
Salicylic Acid
B
Aspirin
B
Saccharine
F
Methyl Salicylate
B
Acetanilide
B
Cresylic Acid
C
Carbolic Acid
C

A FEW OF THE MANY HUNDREDS OF COMPOUNDS THAT THE CHEMIST HAS MADE FROM COAL

The letter A (on the bottle) signifies that the compound named on the label is a dye; B a medicine; C a disinfectant and antiseptic; D an explosive; E a food preservative; F a sweetening agent

Chemistry AT WORK

By

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PREFACE

A preface is a device invented to give an author a chance to tell why he has written a book. If the book is a text, the author is further afforded the opportunity to describe what he considers to be the essential qualities of such a book. About a text in chemistry, designed for use in a high school, the present authors have very definite ideas growing out of long experience in dealing with elementary students in chemistry and writing texts for them. Their purpose in writing this new text is to carry these ideas into effect as far as in them lies. To their mind the requirements of a good text in any science are these:

The text should leave a lasting impression that a science is the outgrowth of observation, experiment, formulation of laws, and proper use of theories; that it is a continuously growing body of knowledge; that in any given field and at any given time it gives us our best understanding of the natural world of matter and energy.

As presented, the details of the science should be interesting in themselves, and as far as possible should be closely related to the practical experience of the student. In no science is this more easily done than in chemistry. Yet these applications should not be carried so far as to make the text a book of recipes, or a mere collection of useful information to the neglect of a really scientific picture of the constantly changing applications of chemistry.

Everyone will agree that a text for immature students should be profusely illustrated, and that every picture or diagram should show very clearly the thing it is supposed to explain or illustrate and if possible raise some questions in the mind of the student. It is equally certain that the language of the text should be easy to understand and interesting to read, and that the vocabulary should not be too far beyond that of the average high-school student. For him (and for everyone else, for that matter) the simplest possible language is the best language. Yet of necessity he will have to learn the meaning of many technical words, all of which

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are carefully defined in a good text; nor should he be wholly freed from the need to turn the pages of a dictionary from time to time. Else how is his vocabulary of good English words to expand?

Every text should be provided with suitable test questions, numerous exercises, and some form of chapter summaries. To the student these serve the purpose of aids to study and for self-examination. If too meager, they fail in helpfulness; if too extensive, the student is in danger of missing the real content of the chapter. Here is a matter requiring judgment on the part of the author.

In recent years there has been a feeling that the student in any subject should be given an opportunity for an occasional review of the fraction of the subject he has recently studied, as well as a chance to make a fresh start on the new material that lies ahead. It has been urged that the instruction between such pauses for orientation should center about some one key idea or topic constituting a natural unit of study. Some studies lend themselves very easily to such a plan. In others a close adherence to a unit plan may be somewhat forced or it may be difficult to limit the unit strictly to one central theme. This is particularly true where the subject as a whole is closely knit and its development in the text and its mastery by the pupil should be a gradual and sequential process.

The authors believe chemistry to be a subject of this latter kind. It is a continuous, interdependent story that could be seriously distorted by breaking it up into a series of separate and somewhat unrelated units. It has been the authors' conclusion, however, that the treatment of introductory chemistry may be cast in unit form, with the advantage of a suitable foreword preceding a given group of closely related chapters together with a natural pause before going forward. Moreover, some units not intimately connected with the main story may, if necessary, be omitted. This is the plan the authors have adopted. They have sacrificed some of the technical features of units for the desirable consistency and continuity in the study of the subject as a whole. It is their hope and belief that serious students of chemistry will find this method both a natural and a logical introduction to chemistry. Certainly it is the authors' conviction that this organization provides the most effective method for a ready understanding of this field of science.

In common with nearly all more recent texts the present one is considerably more extensive in numbered pages than were former ones. Actually, the factual chemical material in this text has not been much extended. The increase in pages is due principally to larger and more numerous illustrations, an easier and less compact style of statement, a more open page, and more material in the appendixes.

Attention is especially directed to the glossary of important chemical terms found on pages 647 ff. This list is based on the study by Dr. Francis D. Curtis[1] of the technical terms used in a large number of textbooks in chemistry for secondary schools. The present authors desire to express here their indebtedness to this interesting study. They are also under obligations to many individuals and industrial firms for the use of illustrations. This courtesy is acknowledged in connection with the illustrations themselves.

The extent to which the authors have achieved their ideals in this text will be decided by those students and teachers who put it to a test.

THE AUTHORS

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[1] Francis D. Curtis, *Investigations of Vocabulary in Textbooks of Science for Secondary Schools*. Ginn and Company, 1938.

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Chemistry
AT WORK

Unit One. The Chemistry of Yesterday and of Today

WHEN one is getting ready to live in another town or in a foreign country, there are many things he wants to know. What has been the history of the new place? What are its traditions? What kind of people live there? What do they think about? What sort of laws do they live under? What do they do for a living and what chances are there for a newcomer?

You are about to move into a new study, the science of chemistry; and many of these same questions are in your minds or will shortly occur to you. Where did chemistry come from? What kind of ideas have its followers held from time to time? What have they thought about the metals they used or the fires they kindled? What are the discoveries that gave them a real start on the road toward the great achievements of the present day? To what extent does chemistry concern our daily life? What opportunities open before a young man or woman who chooses to become a resident in this city of ideas and chemical activities?

This unit, comprising two chapters, attempts to answer many such questions, and so prepares the way for entrance into the new country of chemistry.

CHAPTER I

The Chemistry of Yesterday

[Alchemy, the Parent of Modern Chemistry]

Our ancestors. Each of us has a long list of ancestors. It extends far back until it is lost in the dim ages of the past. In a similar way each art and handicraft and science has a line of ancestors. Since we are now beginning the study of chemistry, it should be of interest to learn something about the ancestors of this science.

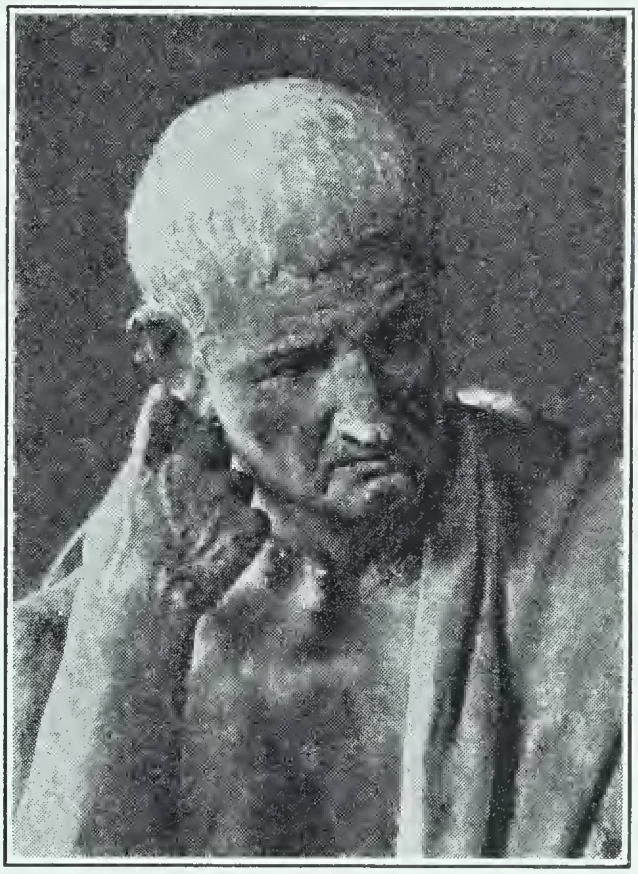


FIG. 1. Aristotle (384–322 B.C.)

One of the greatest of Greek philosophers. He insisted that our knowledge of nature must be gained by observation

What the Greeks gave to science, particularly to chemistry. At first glance we might not recognize our inheritance from the Greeks as belonging especially to chemistry, because it really belongs to all science. But since chemistry was one of the earliest of the sciences to develop, it may lay special claim to this heritage. Let us think, then, of three things we owe to the Greeks.

1. *A great curiosity* about the workings of the world we live in. Most other ancient people were content to take the world as they found it, devoting themselves to useful arts and crafts and to practical affairs. But from very early times Greek teachers (called *philosophers*) wanted to know why things are as they are, why they are continually changing, what becomes of the things that seem to disappear. And as time went on they noticed more and more carefully what was going on in the world about them. One of the greatest of these philosophers was Aristotle (Fig. 1). He wrote about many things, especially about plants and animals.

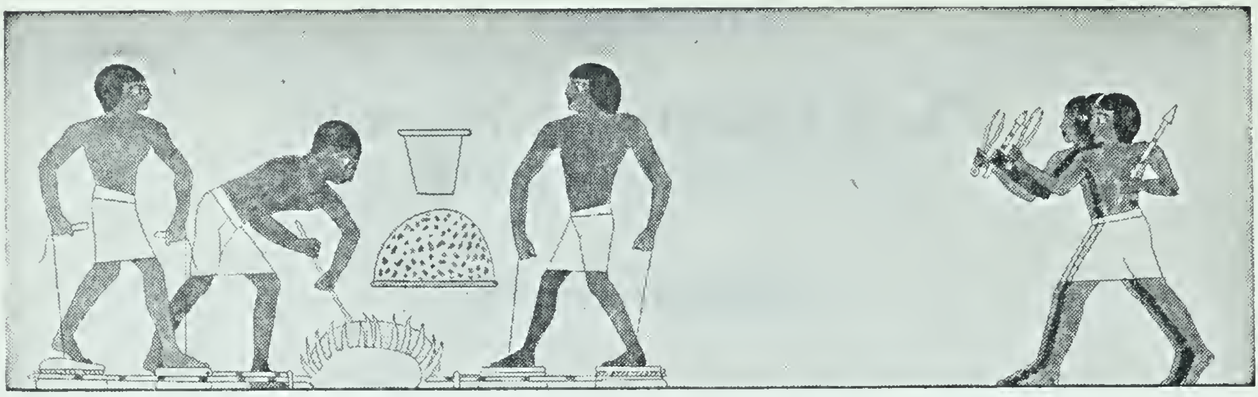


FIG. 2. Thirty-five hundred years ago, the Egyptians worked with metals. Two men are using the bellows to get a hot fire

2. A realization of the fact that we cannot find the answers to such questions without *a very lively imagination and very careful thinking.* This statement will give many of you a new idea about the use of imagination in scientific studies. But although the Greek teachers argued much, and came to a variety of interesting conclusions, they did little in the way of making experiments to test their thinking. They preferred to try reasoning things out.

One of their favorite questions was, How are things made up? They could imagine breaking a stone in two, and each half again in two. Could that be kept up indefinitely? Some thought it could. Others said: "No; a stone is like a sand bank. You can keep dividing it until you come to a single grain, but you cannot divide that and have sand." In other words, they came to the conclusion that matter of any kind is made up of tiny particles like grains of sand that cannot be further divided. These they called *atoms*, a word that means "indivisible." They could find no way to prove who was right and who was wrong about any such questions; but in arguing about them they developed wonderful powers of close reasoning.

3. A third important idea, that of *elements.* The Greeks thought it could not be that the countless things making up the world, such as oceans, clouds, trees, and rocks, should be wholly different in material. There must be much in common among them. And so presently they arrived at the idea that a rather small number of really different kinds of stuff go to make up objects. These they called *elements.* They thought there were four of these fundamental elements, namely, earth, air, fire, and water — a strange choice to hit upon, it strikes us. And they thought the difference in

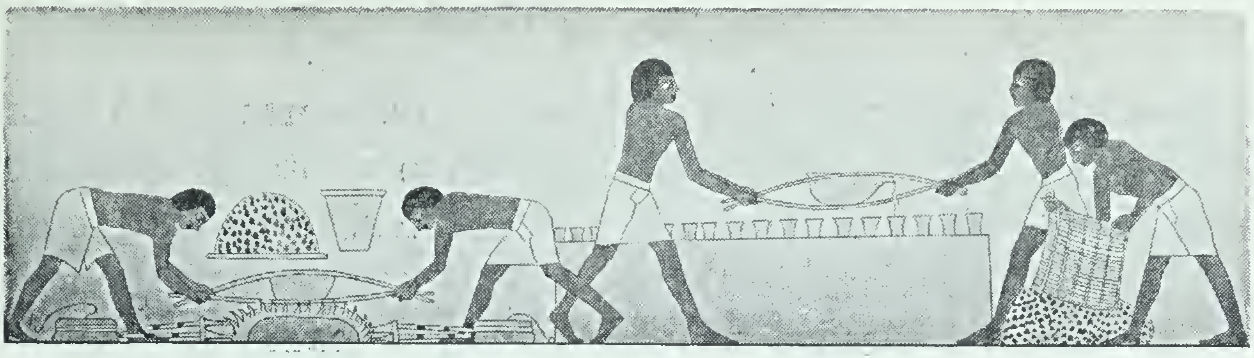


FIG. 3. In this picture two of the workers melt the metal, two others pour it into molds, and one brings fuel

objects was due entirely to the proportion in which these elements were present. With these four in different proportions, they felt they could account for the make-up of almost anything. Much of this thinking we have long outgrown. But we have kept the very important idea that in their vast variety the objects about us are, after all, composed of a relatively small number of unit "building blocks." It is these building blocks we today call *elements*.

What the Egyptians gave to chemistry. The Egyptians, unlike the Greeks, troubled themselves very little about the nature of the world, and busied themselves with the practical side of life. *They excelled in handicraft* — in working in metals (Figs. 2 and 3), glass, and enamels. They also gathered together great books (papyri) of recipes for all sorts of purposes. Many of these had no value. Some described fraudulent methods such as making copper look like gold, while others had to do with religious ceremonies. A few have come down to us because they describe really useful discoveries.

When Greek scholars came to Alexandria about 300 B.C., there was an interesting union of Greek thinking with Egyptian handicraft that resulted in real experimentation. For example, the librarian at the famous library at Alexandria calculated the circumference of the earth from actual measurements, and his results differ only a little from the figure that we now know to be correct. So to some extent the *Egyptians gave us the idea of experiment*, or practical tests, as a check upon imagination and reasoning.

Those mysterious workers the alchemists. During the Middle Ages, and until the Revival of Learning in the fourteenth and fifteenth centuries, the chemists of the time were called *alchemists*. They were chemical descendants of the Egyptians rather than of the Greeks, and busied themselves with many practical problems. They surrounded their workshops with an air of mystery, often wrote in terms no one could readily understand, and claimed to be able to do all sorts of unbelievable things. So they were often thought of as wizards. Artists have delighted to paint pictures of the alchemist (see plate opposite page 8) with a long, white beard, working in his smoky laboratory, with its forge, its crucibles, and its strange apparatus. Many of such paintings adorn the walls of the great art galleries.

What metals did the ancients have? Men have always eagerly sought for metals. Yet as recently as when Columbus discovered America, not more than nine or ten metals were known, although six of them had been widely used for at least four thousand years. These were gold, silver, copper, tin, lead, and iron. Of these gold and silver were found in a natural state in the ground as metal grains or nuggets. The others were got from heavy, colored stones, or ores, no doubt at first by chance as a result of the heat of camp fires, and then by long years of slowly improving methods.

The alchemist's ideas about metals. We naturally think of iron and copper as two entirely different metals, because we have been told this is a fact. The alchemist thought differently. He believed that all metals were really one. Metals seemed to him to be of several different kinds because they had varying degrees of purity. He reasoned that the reddish-brown stone which we now call iron ore was very impure iron. By methods of treatment that had long been used, he knew this stone could be purified into iron. Why, he thought, should not iron, by further purification, become tin or silver or even gold. He called this the *transmutation of metals*; and for centuries he tried to bring it about.

Were the hopes of the alchemists foolish? Many known facts seemed to encourage the idea that one metal could be changed, or transmuted, into another. For example, three thousand years before Christ, men learned to melt copper with a little tin, and so make bronze. This was harder than tin and was yellow like gold. They regarded tin as a medicine that changed the nature of copper. Then, too, the alchemists were ignorant of the fact that many lead ores contain a little silver. In working such ores they first obtained what seemed to be pure lead, but by further refining processes they got silver from this lead. They then thought that some of the lead had been transmuted into silver.

The alchemists failed. Until about the seventeenth century the alchemists continued this vain endeavor before they were convinced that transmutation of metals was impossible by any means within their power. So eager had been the hope, however, that many kings had employed gold-making alchemists, and even the great Sir Isaac Newton, beginning about 1700, spent years of his life in this fruitless endeavor. It took a long time to prove that every metal is really different from every other one; but we may well remember that it took longer still to prove that the earth is round and not flat. Today we can bring about minute transmutation of certain metals, but not by methods dreamed of by alchemists.

The "elements" of the alchemists. Toward the end of the Middle Ages the alchemists began to differ among themselves about the so-called elements. Many preferred sulfur, mercury, and salt to the earth, air, fire, and water of the Greeks. Sulfur represented the part of any material that could be burned; mercury, the part that passes into a vapor, or gas; salt, the ash that remained after burning. To say that a thing contained lots of sulfur meant to them merely that it burned easily.

The language of the alchemists became more vague and mysterious, and curious pictures were in common use to express chemical ideas. The metals were represented by the stars, planets, sun (gold), and moon (silver), or by animals (Figs. 4 and 5).

The philosopher's stone the alchemists' last hope. Failure always followed honest efforts to change one metal into another. Of course, many fraudulent claims were made, just as perpetual-motion machines and cancer cures have been advertised even in these later days. Rather than give up hope of making gold from a cheaper metal, such as copper or mercury, many alchemists came to believe that this could be done only by the wonderful power of a magical substance

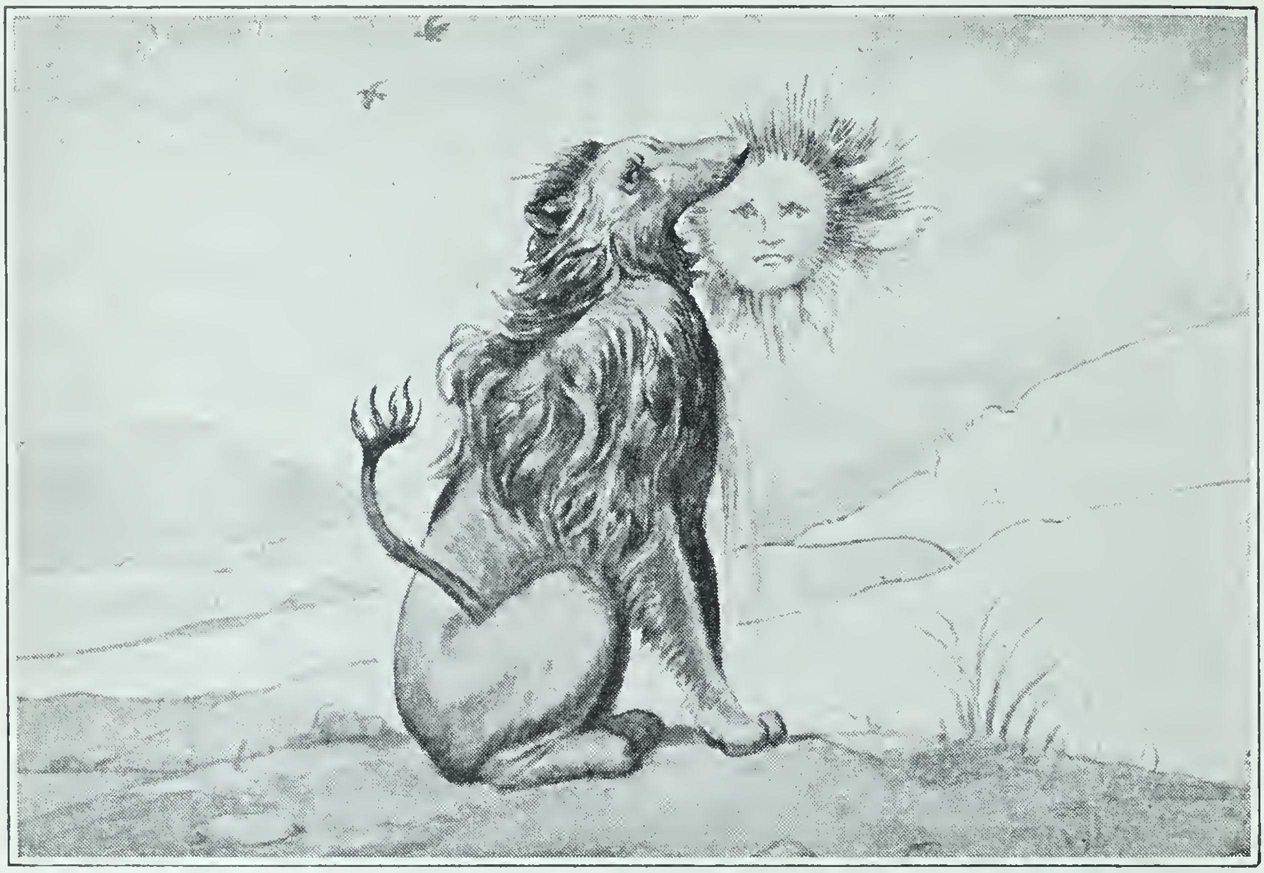
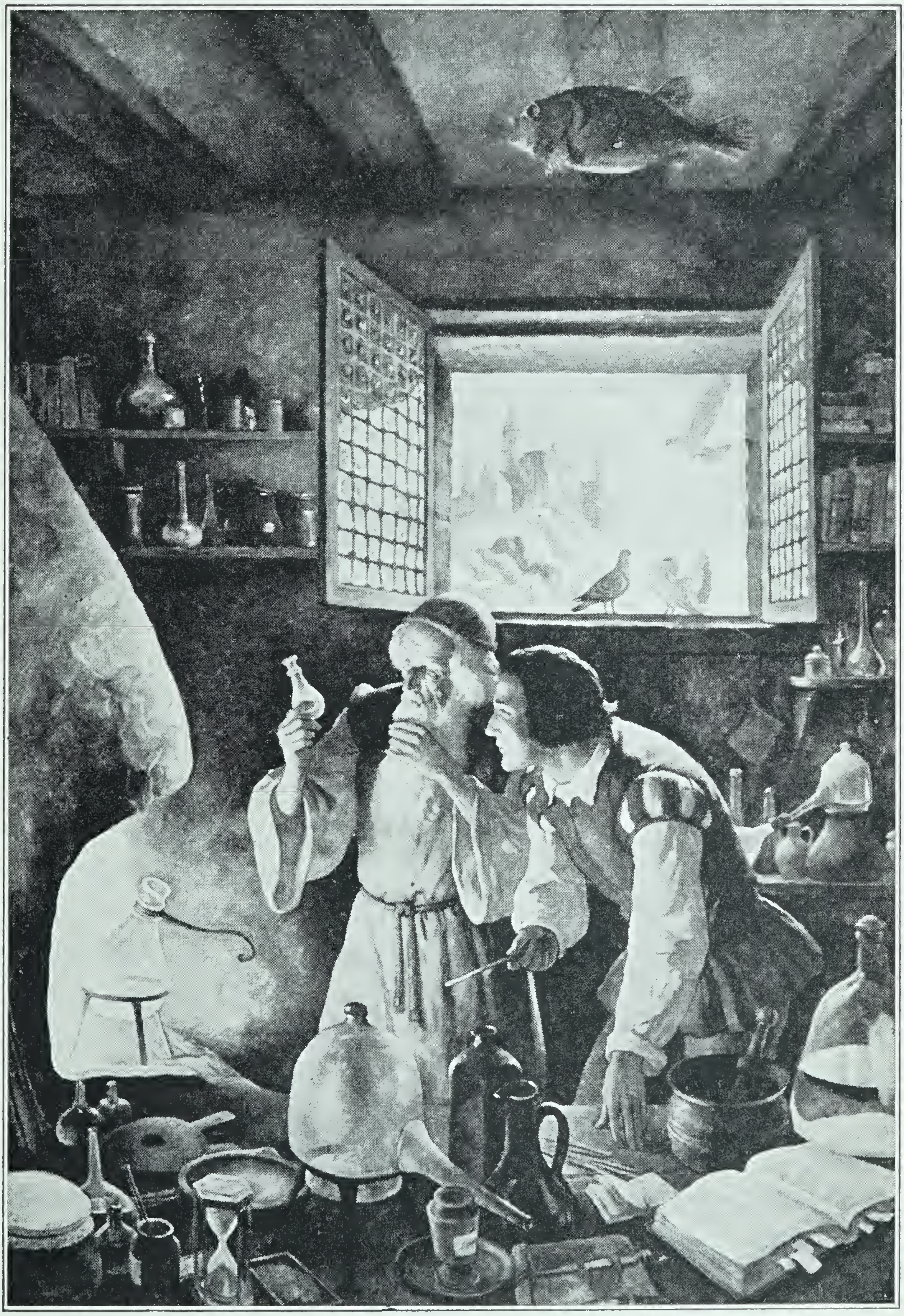


Fig. 4. The lion (mercury) devouring the sun (gold), illustrating the fact that mercury dissolves gold

which they called the *philosopher's stone.* Different ways were described for making or finding this wonder-worker. Its reputed powers increased as the alchemists felt baffled in their efforts. So they assumed that if you could get this precious stone, its mere touch would solve all problems and change untold quantities of mercury into gold. They also thought it would cure all diseases, and give perpetual youth to its fortunate possessor. So it was sometimes called the *elixir of life.* It was thought to be even more wonderful than Aladdin's lamp in the Arabian Nights.

Does chemistry owe anything of value to the alchemists? By the eighteenth century alchemy was fast becoming a discredited art. So we may ask whether the many experiments made in the alchemist's workshop resulted in anything of value that has been handed on to us.

First of all, their failure to find a way to transmute metals was finally accepted as proof that each metal is an individual thing that cannot — at least by chemical means — be changed into another. In addition they discovered a few metals unknown before (antimony and zinc), and the nonmetals arsenic and phosphorus. They made a considerable



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The Alchemist

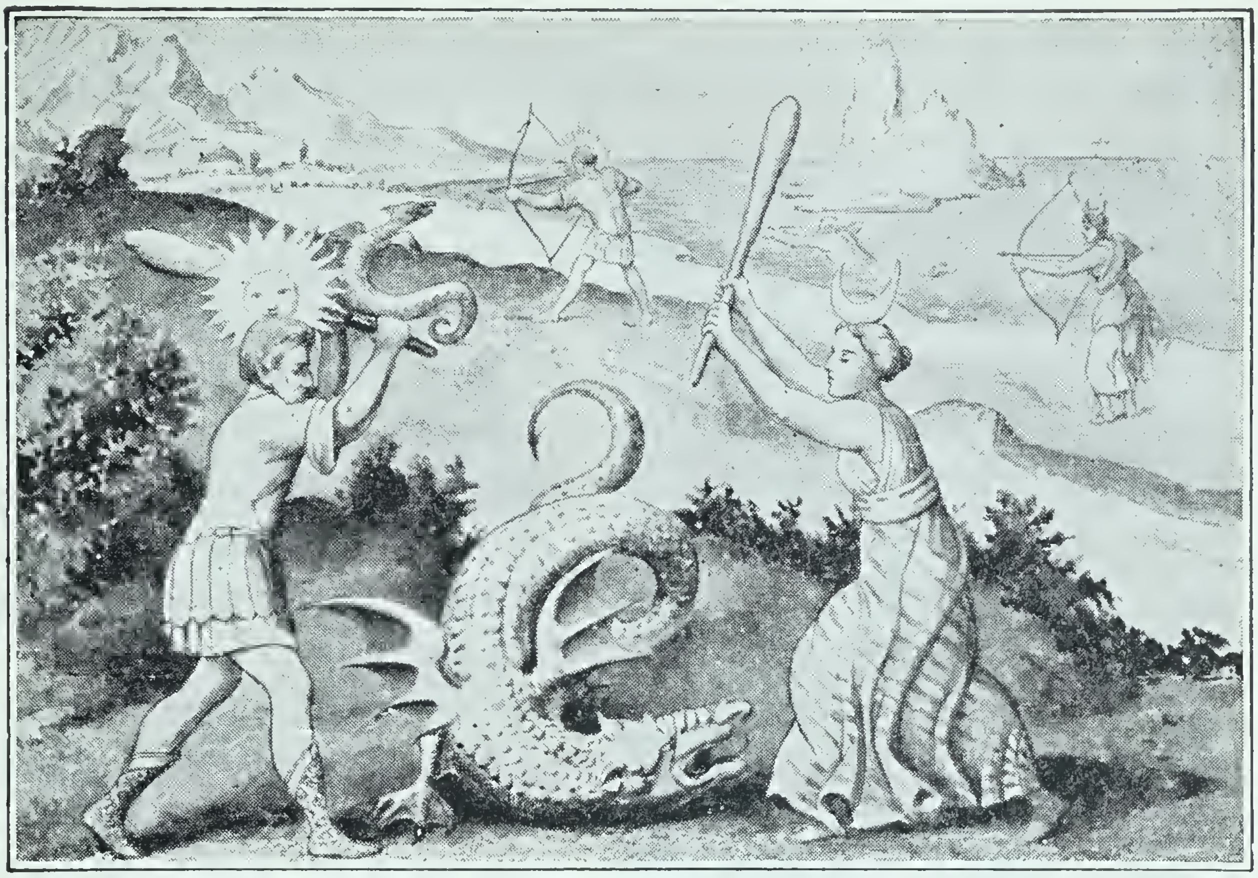

FIG. 5. Gold (the sun) and silver (the moon) being combined with mercury (the dragon) to make the philosopher's stone

number of new and useful chemical substances. They improved such industries as metallurgy, glassmaking, and dyeing. Finally, they developed many processes that we use today, such as distilling, filtering, and grinding, and the beginnings of modern laboratory experimentation.

What makes a thing burn? By the beginning of the eighteenth century the alchemists had disappeared. Their place was taken by those we would today call physicians, druggists, and teachers. To these men the greatest mystery within their observation was this: Why do some things burn while others do not? What makes a thing burn? Now, when we cannot find a ready answer to such a question, we are inclined to create a new mystery to explain the old one. We invent a mysterious ether to carry waves of light because we think that waves have to move in something; and we invent an electrical fluid, or two of them, to explain electrical currents.

Phlogiston. In this way the German writer Stahl (Fig. 6) invented a chemical fluid to explain burning, and his ideas were generally accepted by the chemists of his time. They called the fluid *phlogiston*, which means simply "the thing that makes things burn." Everything that burns, they reasoned, contains some of this phlogiston. When the material burns, this phlogiston escapes, causing crackling, small explosions, sparks, flames, and smoke, leaving behind an ash. But many things, such as candles and oils, burn without leaving an ash, and these were thought to be nearly pure phlogiston.

Fig. 6. G. E. Stahl (1660–1734), who originated the idea of phlogiston to explain burning

While the phlogiston idea explained many things, it failed to account for others. For example, the ash of coal weighs less than the original coal, and this could be satisfactorily explained by assuming that the phlogiston that escaped during the burning has weight. But when iron burns, the ash weighs more than the original iron; and this could not be explained in any reasonable way. So the idea of phlogiston led to many difficulties and contradictions.

The great discovery of chemistry. For nearly a century chemists tried to make the idea of phlogiston agree with the experimental facts of burning. They could not do this, nor could they think of a better explanation. Then in 1774, just two years before the beginning of the American struggle for independence, Joseph Priestley (Fig. 52), an Englishman (who afterward became an American citizen), discovered oxygen. It then became possible not only to explain burning but to lay the foundations of chemistry as we have it today. We now turn to the study of this modern chemistry based largely on oxygen, our most abundant element. But let us not forget the patient work of all those who, through the centuries, prepared the way for our understanding.

CHAPTER SUMMARY IN QUESTION FORM

1. Name three important things that we owe to the Greeks.

2. Tell what the Greeks understood by the following words: (*a*) atom; (*b*) element.

3. What contributions did the Egyptians make to chemistry?

4. Contrast the contributions made to chemistry by the Egyptians with those made by the Greeks.

5. What metals were known to the ancients?

6. By what name were the early chemists known?

7. Contrast the alchemists' ideas about elements with those of the Greeks.

8. What ideas did the alchemists hold in regard to the metals?

9. Mention some facts that led the alchemists to believe in the transmutation of metals.

10. Tell what is meant by the following terms: (*a*) the philosopher's stone; (*b*) the elixir of life.

11. What contributions did the alchemists make to chemistry?

12. What is the meaning of the word *phlogiston*?

13. How did those who believed in phlogiston explain the fact that some substances burn while others do not?

14. What great discovery ended the belief in phlogiston?

THOUGHT QUESTIONS

1. Some of the Greeks thought that matter was infinitely divisible, while others thought not. Considering the knowledge of that time, which side would you take?

2. Do you think it reasonable to believe in a thing like phlogiston, whose existence cannot be proved?

3. Were the alchemists honest in their beliefs or were they fakers?

4. Why do you think the alchemists reported their discoveries in such vague and mysterious language?

5. Suppose that some simple method were to be found for transmuting a cheap metal like lead into gold. What do you think would be some of the results of such a discovery?

OPTIONAL EXERCISES

1. Try to find out the origin of the word *chemistry.*

2. Report interesting facts about three distinguished persons mentioned in this chapter. (Consult an encyclopedia.)

CHAPTER II

The Chemistry of Today

[What Chemistry Is and What the Chemist Does]

Some questions to be answered. The main question that the student just beginning the study of chemistry will ask, or should ask, is, "What is chemistry, anyway?" He has often heard the word used — perhaps used it himself. He knows that there are many teachers of chemistry and that many firms employ chemists. But just what chemistry is and what the chemist does may not be so clear in his mind. It is important for the student to have this information at the beginning of his study of chemistry. It is the aim of this chapter to answer these questions.

Chemical changes. Every day, if we keep our eyes open, we see wonderful changes taking place in everything about us, although we may pay little attention to them. We know how hard it is to keep iron tools or motorcar fenders or the kitchen stove from rusting, or silverware and brass ornaments from tarnishing. We fill the tank of our motorcar with gasoline; but when the motor is started, the gasoline is changed into gases that are burned in the engine. A log of wood burns and ashes are left. The food we eat is changed into blood, bone, muscle, and other structures that make up our bodies, and is burned to keep them at the right temperature and enable them to do work. Plants of all kinds take simple materials from the soil and air and build them up into complex tissues as they grow.

In all these illustrations *the materials with which we start are changed into others of entirely different composition.* All such changes are called *chemical* changes. The chemist is particularly interested in them.

A chemical change is a change in the composition of matter.

Slow and fast changes. Chemical changes may take place with various degrees of rapidity. Some take place so slowly that we do not observe them, as is the case of the rusting of iron or the breaking down of rocks into soil

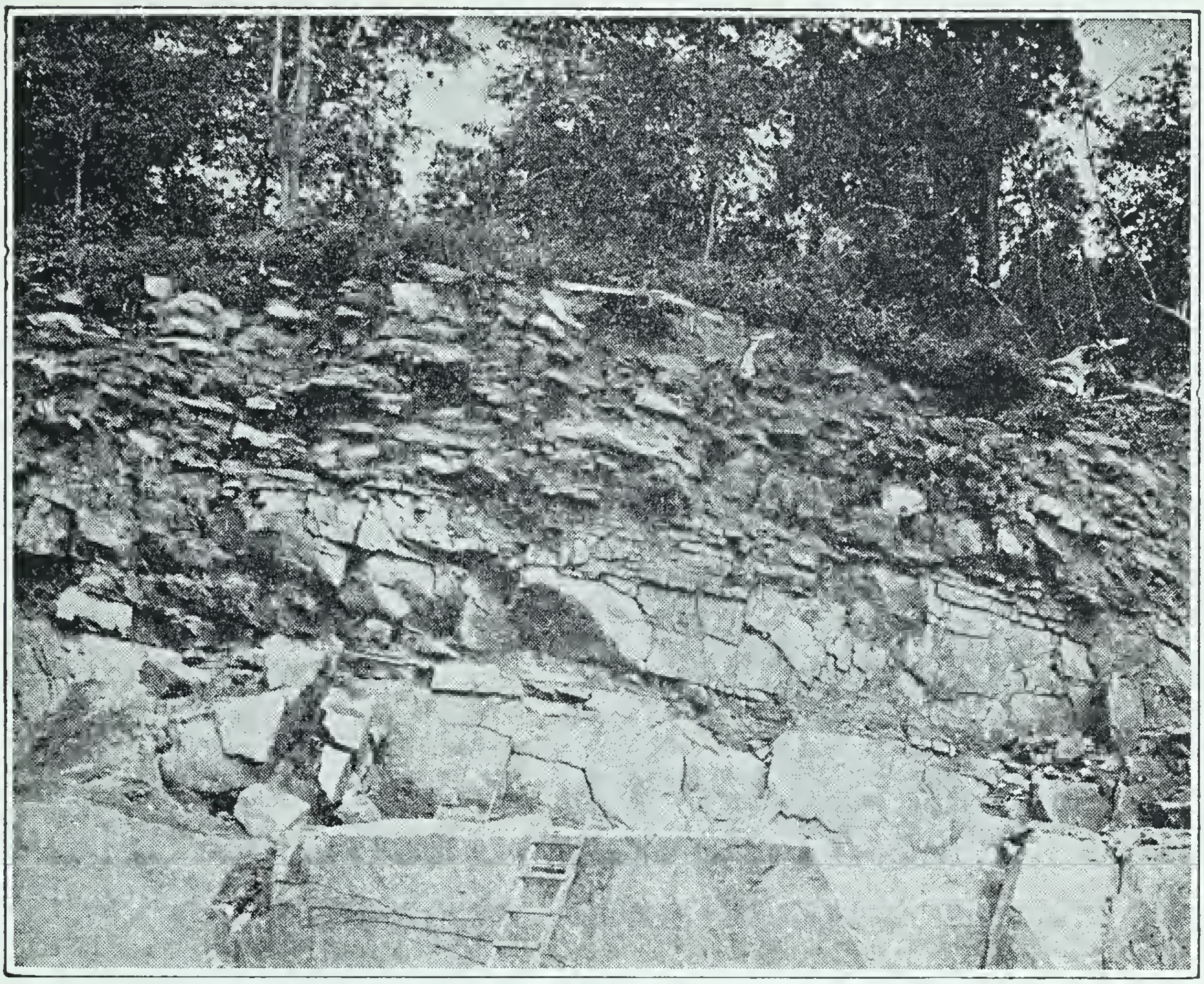

FIG. 7. A slow chemical change. This picture shows rock being broken down into small stones and soil by the action of air and water

(Fig. 7). Others, such as the burning of a candle, take place more rapidly; and still others take place instantaneously, as in the explosion of dynamite or gunpowder (Fig. 8). In all such changes heat is always given off or absorbed, and often, in the case of rapid changes, light is given out as well.

Physical changes. But there is another kind of change, in which the material is not changed in *composition.* We may break a dish or pane of glass into pieces, pound a lump of coal into dust, or split a log of wood into kindling. By doing this we do not alter the composition of the original material, only its form. Each little particle has the same composition as that of the object from which it came. All such changes are called *physical* changes. They are of less importance to the chemist.

A physical change is one that does not result in a change in the composition of matter.

What chemistry is. Having clearly in mind just what is meant by *chemical change*, we are now ready to make a definition of the subject of our study.

Chemistry is the science that deals (1) with the composition of materials and (2) with all those changes in materials that alter their composition.

For example, the chemist has little interest in the breaking of a lump of coal into pieces; but he is deeply interested in its composition and in the changes that take place when it burns.

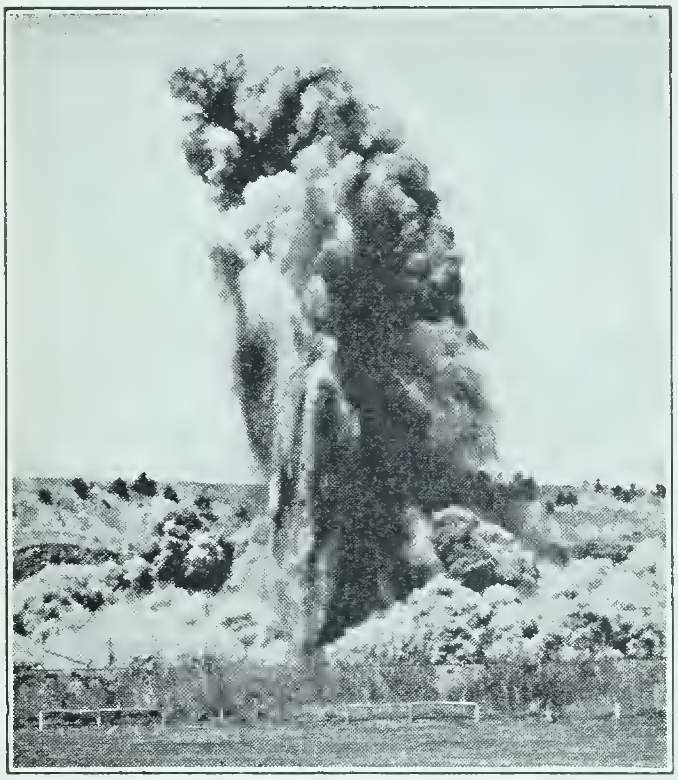

Fig. 8. A swift chemical change. The explosion of a charge in a quarry

Before the chemist began his work. The life of primitive man was almost unthinkably crude. Nature had given him the bare necessities of life in the fruits, berries, and seeds he found at hand and in such animals as he could capture. His rude handicraft gave him chipped stones as tools, made him cloth of coarse fibers, and shaped him sun-dried bricks and pots. He went so far as to hammer together grains or flakes of gold or of copper, and from these larger pieces he made ornaments (Fig. 9), tools, and weapons. This was about as far as he could go without learning how to change in some way nature's raw materials.

New materials from living things. We have overlooked the greatest gift nature gave to man — an imaginative, creative brain. With this he very early set to work to improve upon nature. His food was his first interest. By cultivation he found he could get better grains than wild grasses gave him; better onions and cabbages and cucumbers than he found growing wild. In fact, he gradually so improved these food plants that today we do not know with what wild plants he started. The Indians grew pretty good corn, but we know of no wild grass that in any way resembles it. This process of improvement is still going on even more successfully than in the past. Not so many years ago a beet had just enough sugar in its root to suggest an idea. The modern beet contains as much as 20 per cent by weight of sugar and is the source of a large percentage of the sugar we use.

FIG. 9. Copper ornaments excavated from the mounds of the mound-builders

Rather than depend on wild animals for meat and milk and wool and eggs, primitive man utilized his brain and began a process of taming and breeding that has resulted in our modern domestic animals, many of which bear little resemblance to their native ancestors. No one would imagine that a lady's lap dog has to acknowledge some sort of wolf as its forefather.

Now in all these changes we can hardly say that man has acted as a chemist. We call him a gardener (or horticulturist) or a stockbreeder. But in reality every plant and animal is a chemical laboratory of nature. Man has merely been nature's able assistant, helping her turn more materials from soil, water, and air into grains, fruits, seeds, meat, milk, and eggs than she could do by her own unaided efforts.

New materials from lifeless matter. While the chemist is deeply interested in the changes that take place in all living things, in our bodies and in growing plants, his chief work has been with the changes that take place or can be made to take place in lifeless matter. He mines ores of various kinds and from them obtains the metals that play such an important part in our lives. From different rocks he manufactures such articles as lime, cement, glass, fertilizers, and paint colors. From coal he makes thousands of dyes of every color, drugs, perfumes, and many less familiar things (see

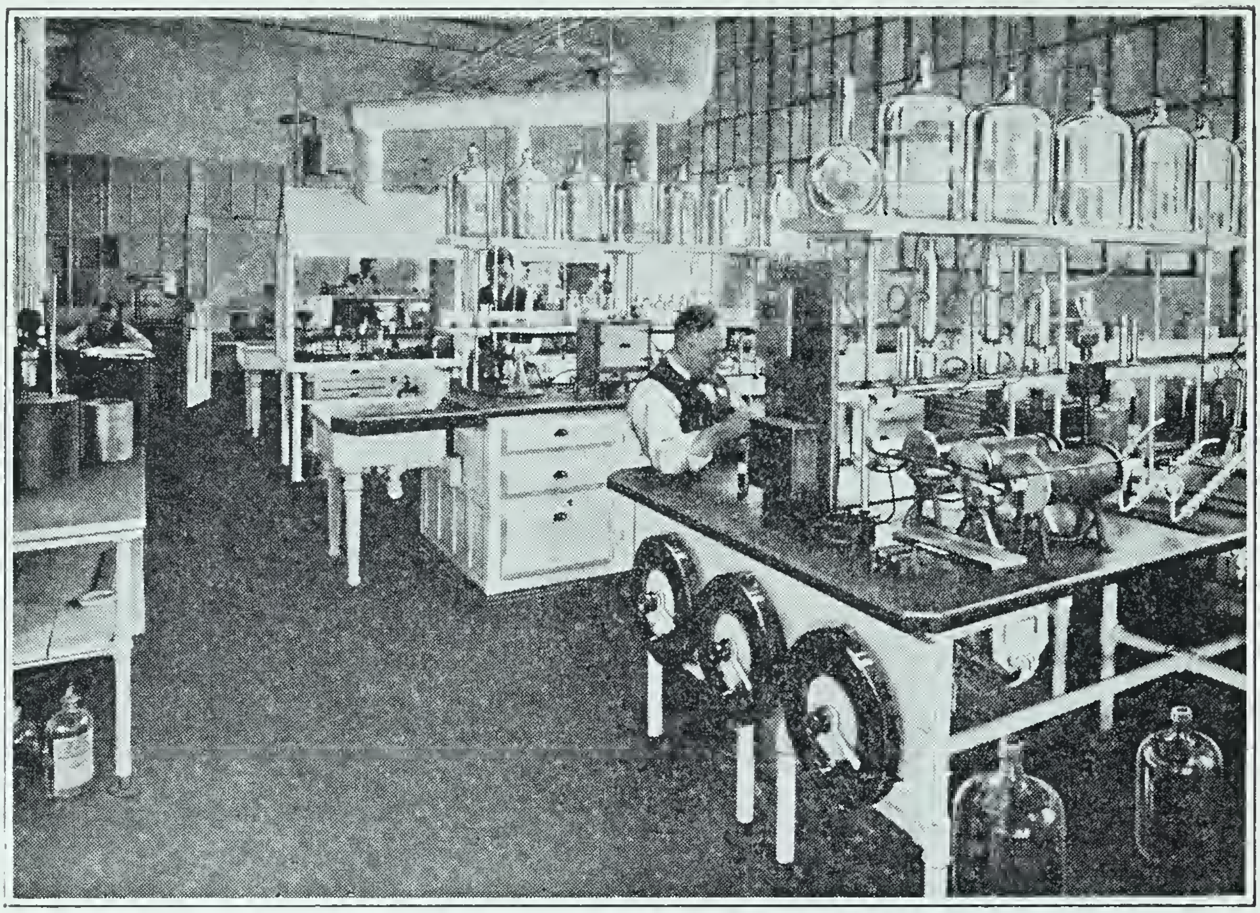

Fig. 10. A typical laboratory of a modern automobile plant, in which every material used in making automobiles is carefully analyzed and tested

frontispiece). From petroleum and wood and the sap of trees, from milk and hides and seeds (Fig. 12), he fashions important things of everyday use. In all these ways and countless others the chemist has been the chief agent in making it possible for even the humble citizen of today to live in greater comfort and in better health than the kings and queens of old.

Chemical industries. Almost all the industries that turn a raw material of nature or the refuse of some factory into a useful product are chemical industries. Someone has said that "there is scarcely an article in common use which does not owe its existence, directly or indirectly, to the application of some chemical principle. Close your eyes, enter any room and touch at random any object, and ninety-nine times out of one hundred, the object will be related somehow to one or more chemical industries." All such industries, if they are to succeed, must be in charge of trained chemists (Fig. 10). Indeed, the *industrial importance* of any country may be judged fairly well by the extent to which chemistry is studied in its schools and colleges (Fig. 13).

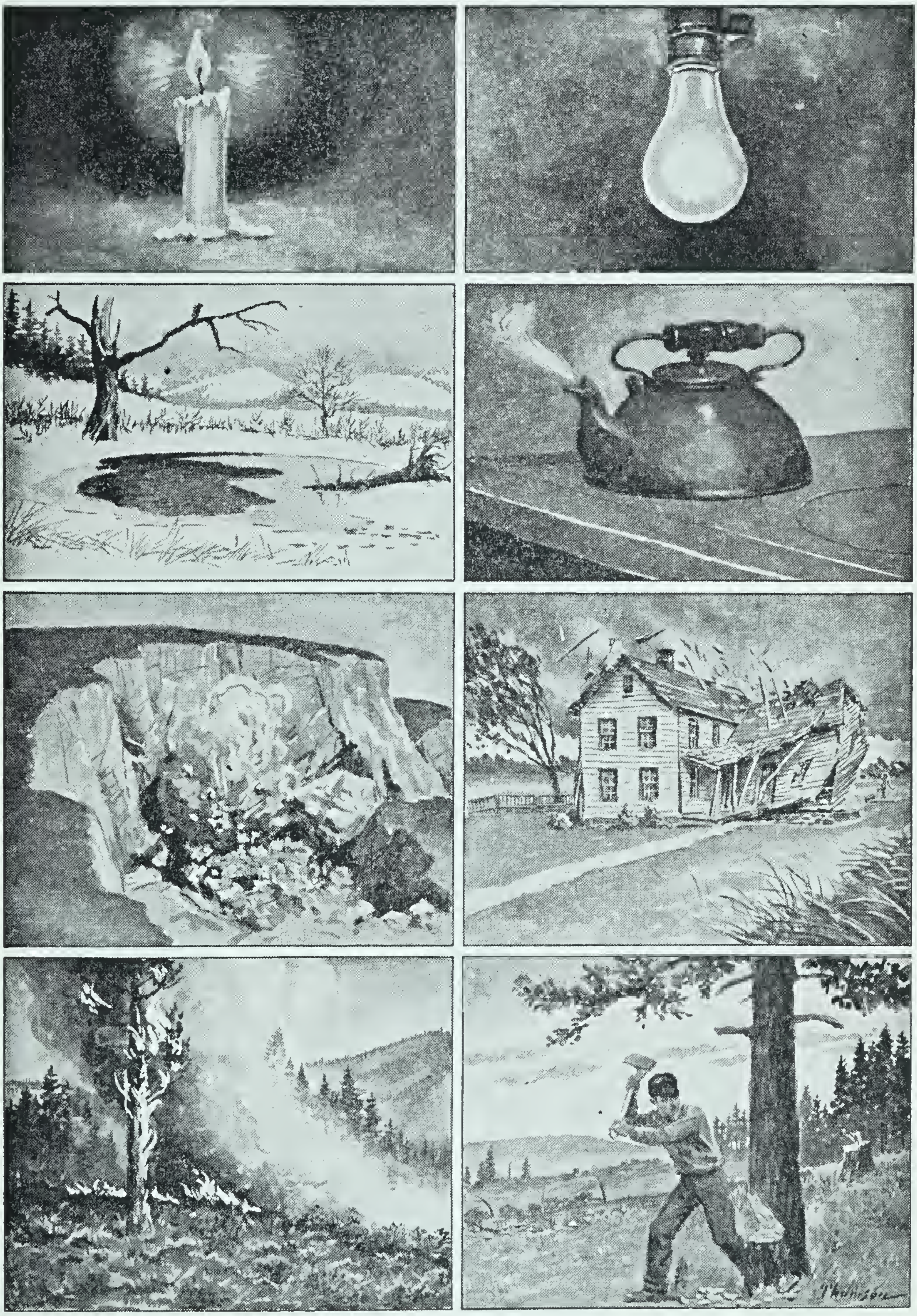

FIG. 11. This figure shows a number of changes taking place. Which are chemical and which physical?

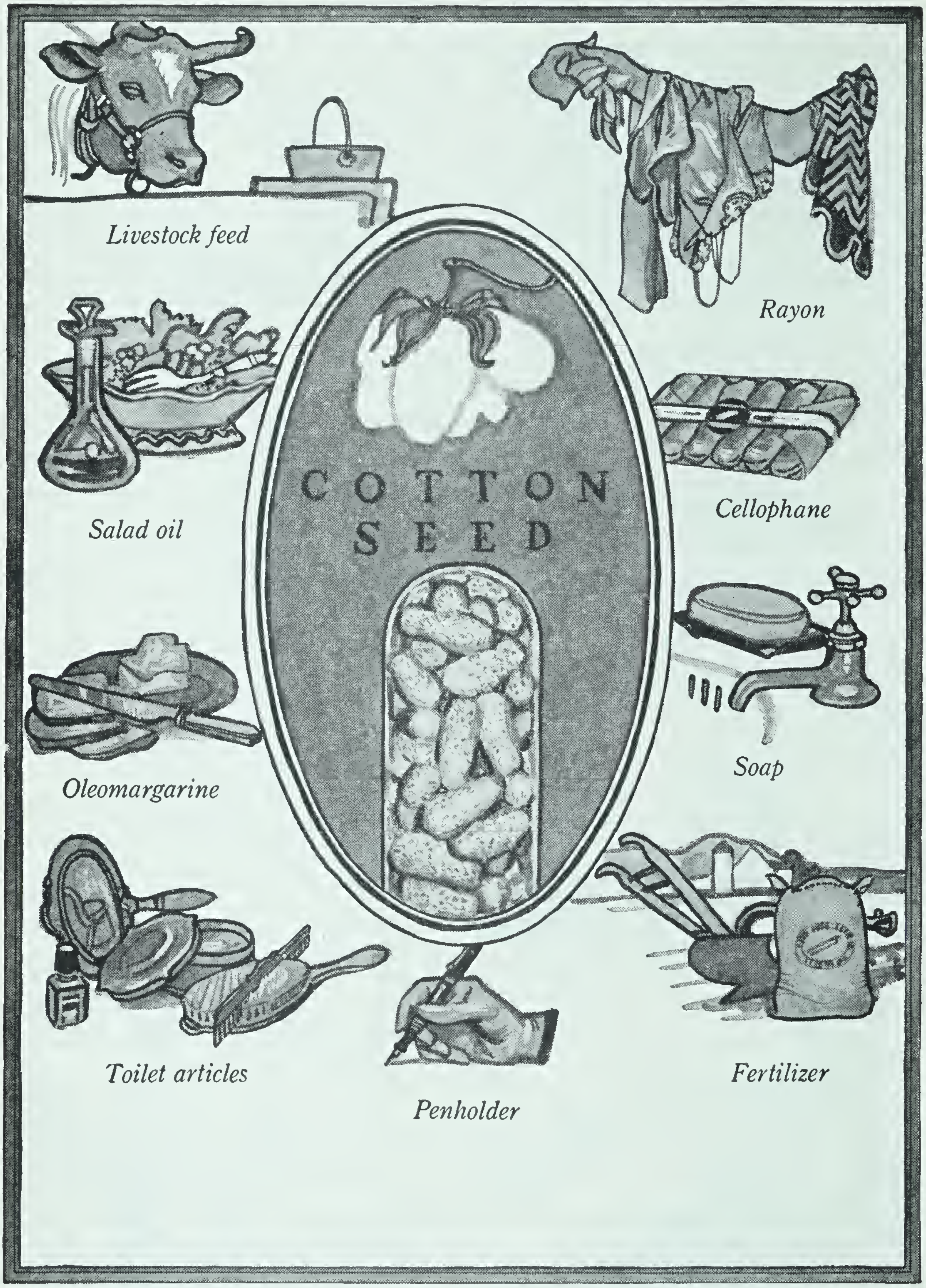
Livestock feed
Rayon
COTTON SEED
Salad oil
Cellophane
Soap
Oleomargarine
Toilet articles
Penholder
Fertilizer

FIG. 12. This picture shows a number of products which the chemist has succeeded in making from cotton seeds

Formerly these seeds were a source of expense, since they were bulky and had to be disposed of in some way. Today they are a source of great wealth, thanks to the chemist

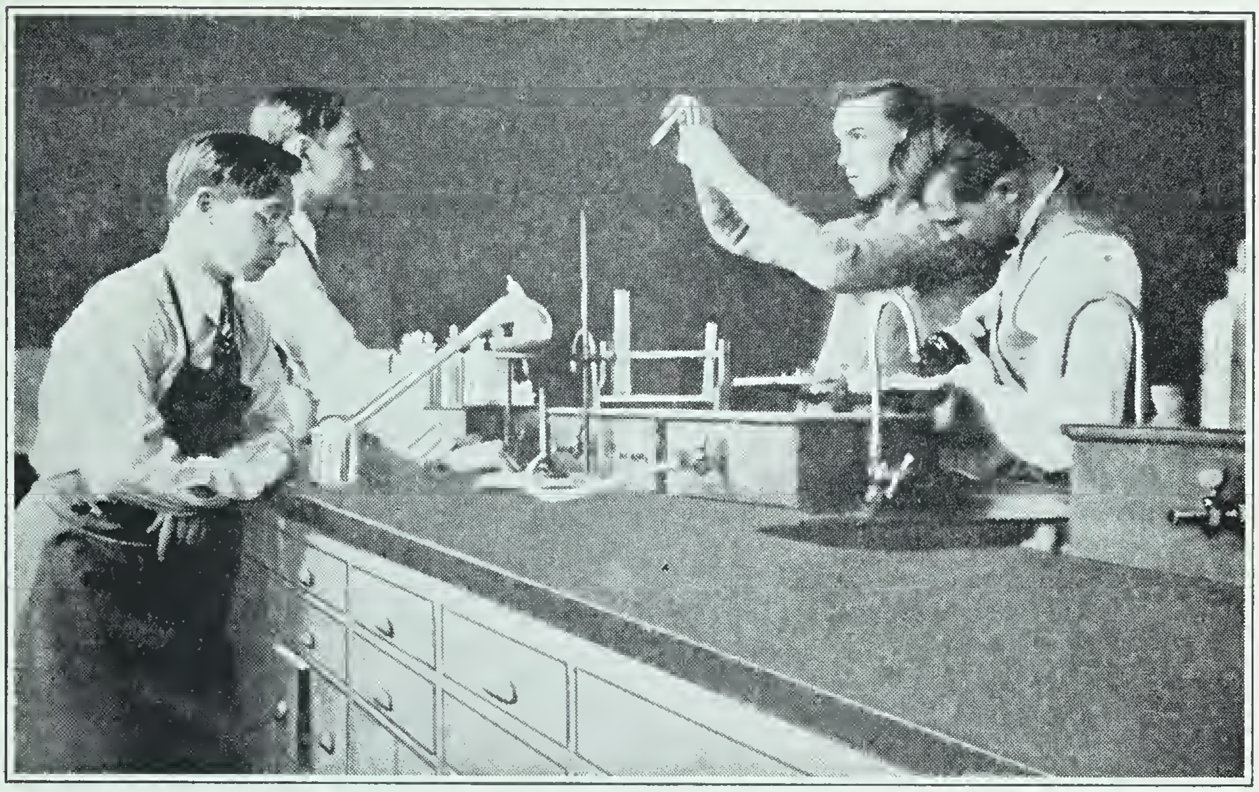

Fig. 13. Learning chemistry in the high school

The chemist in charge of an industry. The chemist is really the scientific leader in the success of his industry. He must watch over all its processes and work out every possible improvement. He must test the value of each lot of raw materials that comes to his factory and modify his processes to fit his findings. He must be able to guarantee the quality of his output so that there may be no question about its coming up to standard. He must study the possibilities of making something useful out of waste materials or making a better article out of other materials than those he has been using.

The chemist in the fight for health. The chemist plays a very important part in our fight for health. Indeed, he provides the physician with most of his weapons. He finds out the kinds and the amounts of food best suited to our bodies. Knowing that many diseases are spread by impure drinking water, he devises ways of purifying our water supplies and getting rid of our sewage. He prepares drugs for fighting diseases, anesthetics for preventing pain during surgical operations, and antiseptics for warding off infection so that a wound will readily heal. The delicate tools used by the surgeon are fashioned under his guidance. He studies the composition of those strange substances that regulate the

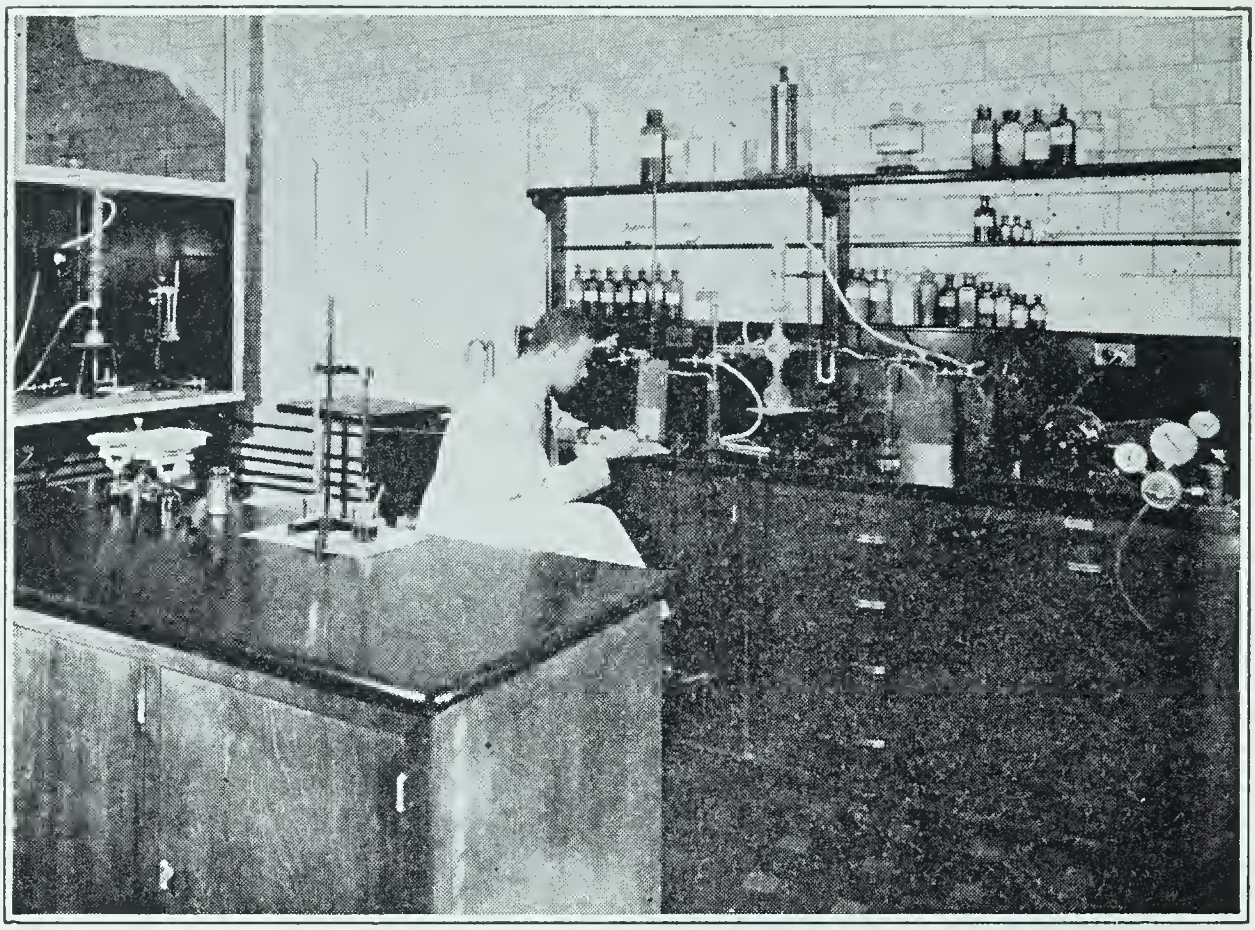

FIG. 14. This is a picture of a room in the large laboratory of Eli Lilly and Co. The whole laboratory is devoted to making and testing medicinal preparations

activities of our bodies, and is learning how to prepare them for the use of those unfortunates who are suffering because their own bodies do not supply their needs. These are only a few of the ways in which the chemist is contributing to the health of the nation (Fig. 14).

Relation of chemistry to other sciences. Many different fields of learning are very closely related. Especially is this true of the sciences. Indeed, one cannot go very far in the study of such subjects as physics, geology, mineralogy, and biology without knowing something of chemistry. The geologist and mineralogist must know the composition of rocks. The metallurgist and mining engineer are really industrial chemists. The biologist must understand the changes that take place in living things. Physics and chemistry are so closely related that textbooks of these two subjects contain much in common. Whatever field of science a student may wish to master, he must know the principles of chemistry and be able to apply them.

Have chemists found out all there is to know? Far from it; indeed, they have only made a good beginning. Every day sees some advance in our understanding of why chemical changes take place. We are learning what kinds of change are possible and what are not. We are constantly improving known methods and finding new materials to put to new uses. Every invention — such as the phonograph, the moving-picture film, the radio, color photography, television — requires some new material that the chemist must be able to supply.

Fig. 15. Charles Martin Hall (1863–1914)

When hardly out of college he solved the problem of cheap production of aluminum. The figure shows a statue of Hall, made of aluminum and presented to Oberlin College, where he made his first experiments and to which he left a fortune

Our knowledge of the changes that take place in growing plants and animals is very limited, although we are learning fast. Plants manufacture sugar, starch, and cellulose from simple materials taken from the soil and the air, but no chemist can yet do this in his most perfectly equipped laboratories. Undoubtedly the farmer will be greatly helped by the further application of chemical principles. Already the chemist has found ways of converting waste farm materials, such as cornstalks, into useful products.

What chemistry offers to youth. Chemistry offers to students many attractions and great variety as a lifework. There is a wealth of problems of the utmost importance to human comfort and happiness that remain unsolved. Large rewards await the ingenious and energetic discoverer (Figs. 15 and 16). Virtually every line of progress increases the number of those taking part in a chemical occupation. In every progressive country the national chemical society is

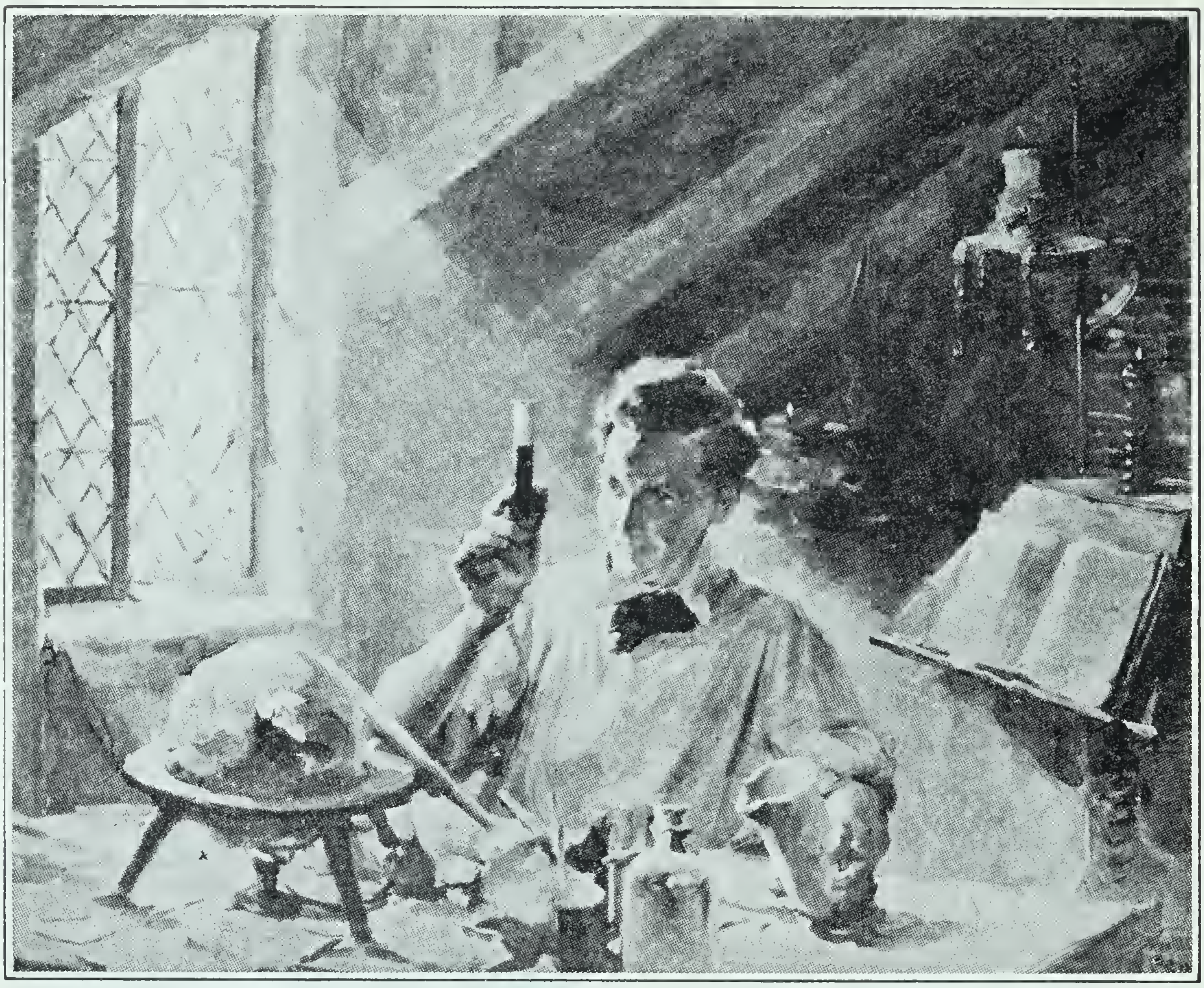

Fig. 16. William Henry Perkin — the boy who found rainbows in coal

"One Easter vacation in 1856, seventeen-year-old William Henry Perkin, a student assistant in the Royal College of Chemistry, was toiling in an improvised laboratory under the eaves of his English home. 'Throw the rubbish away,' croaked unimaginative Common Sense when the boy poured in a red fluid and got a sticky dark mass at the bottom of his test tube. 'Examine it,' whispered Science; 'it may be worth something.'" Science was right. Out of that ugly dark mud came a lovely violet-purple dye — "mauve," the first aniline dye made from coal tar. (Courtesy of Parke, Davis and Company)

one of the largest of its scientific organizations. The American Chemical Society has about twenty thousand members.

A final question: What is science? We have referred to chemistry as one of the sciences; and the question arises, "What do we mean by this word *science*?" As a matter of fact, the word is not easily defined, and it is often used in a rather loose way. It is certain that mere knowledge does not constitute a science. If it did, then alchemy would have to be called a science, for the alchemists possessed a knowledge of many facts.

What was lacking to make alchemy a science was the proper classification and use of this knowledge in such a way as to make it of value in the search for new facts. The discoveries that alchemists made were largely the result of chance. The chemist, on the other hand, has now available a body of classified and tested knowledge which he can use in devising experiments and directing them toward some result he hopes to obtain.

Science is a body of knowledge classified in such a way as to make it of value in the search for new knowledge.

NOTE. *In this text the temperature readings will be in the centigrade system, and the metric system of weights and measures will be used unless otherwise noted. Students not familiar with these units will find an ample explanation in the Appendix.*

The usual abbreviations will be used: C *for* centigrade, *and* F *for* Fahrenheit (*in case the latter is used in special cases*); m *for* meter, *and* km *for* kilometer; g *for* gram, *and* kg *for* kilogram; ml *for* milliliter. *Some authors prefer to use the cubic centimeter* (cc) *in place of the milliliter. The two units are identical, but the latter term is preferable and is coming into general use.*

CHAPTER SUMMARY IN QUESTION FORM

1. (*a*) Define two important kinds of changes. (*b*) Which of these is of special importance to the chemist? (*c*) Give examples of each kind.

2. Mention two subjects with which the science of chemistry deals.

3. What is the source of all the raw materials which civilized man uses?

4. How does a knowledge of chemistry help one to understand other fields of study, such as agriculture, biology, geology, and physics?

5. Mention a number of chemical industries.

6. What part does the chemist play (*a*) in most industries? (*b*) in preserving the health of the people?

7. Enumerate some of the problems that have yet to be solved by the chemist.

8. What is meant by the word *science*?

9. Name two very important discoveries made by young men when they were students in college or had just graduated.

THOUGHT QUESTIONS

1. How do you account for the fact that you can get sugar from beets, and rubber from trees, but that you cannot get gold from iron?

2. Give reasons for the statement that the human body is a chemical laboratory.

3. What products can you name that are derived (*a*) from the sap of trees? (*b*) from milk? (*c*) from hides of animals? (*d*) from the earth? (*e*) from the air?

4. Mention some of the materials and objects in your home in the preparation of which chemistry has played a part.

5. Mention and classify as physical or chemical some of the changes you have observed during the day.

OPTIONAL EXERCISES

1. If there are any factories in your locality that employ chemists, select one or more of them and find out just what their chemists do.

2. (*a*) Find out what the city or town in which you live is doing to preserve the health of its people. (*b*) Does it have a "health officer"? If so, find out what his duties are.

UNIT READINGS

Each student should read one or more of the following references and either report interesting facts to the class or write a brief review of the reference.

Note. A list of the books to which references are made in the text, together with the name and address of the publisher of each book, will be found in Appendix A.

Darrow. *The Story of Chemistry.* [Read Chapter I, "The Alchemist"; also Chapter XIII, "Chemistry in the Day's Work."]

Foster. *The Romance of Chemistry.* Chapter I treats of "Alchemy and the Rise and Development of Chemistry."

French. *The Drama of Chemistry.* [Chapter I gives an account of alchemy. Chapter VIII deals with "Chemistry and Civilization," and Chapter IX with "The Chemist and His Work." The chapters are written in simple language, and the student will find them of great interest.]

Huxley and Andrade. *More Simple Science.* [Read Chapter VII, "The Improvement of Living Things."]

Leonard. *Crusaders of Chemistry.* [Read Chapter III, "Alchemy."]

Noyes and Noyes. *Modern Alchemy.* [Read Chapter I, "The Methods of Science."]

Slosson. *Creative Chemistry.* [Interesting facts about Perkin (Fig. 16) will be found on pages 72–73, and about Hall (Fig. 15) on page 247.]

Weeks. *The Discovery of the Elements.* [Read Chapter I, "Elements Known to the Ancient World"; also Chapter II, "Elements Known to the Alchemists."]

The World Book Encyclopedia (excellent for secondary schools) contains an interesting article on "The Story of Chemistry."

Unit Two. The Make-up of the World: Matter and Energy

IT IS interesting to notice the materials a contractor gathers together when he is about to start on a new building. We see piles of building stone and crushed stone, of brick, of sand, of rough lumber; sacks of cement and of lime; rods of iron; an engine to move these things about.

Some of these materials will be used in every part of the main structure of the new building. They are *general* building materials. Later on, the contractor will have to think about very *specialized* things: glass of the right size for windows, suitable locks and hinges for doors, the right coloring for the walls, and the finish of the woodwork.

So too in chemistry. Before we begin the study of particular elements and compounds, we must gather our chemical material into general classes, as the contractor makes separate piles of his building materials. We must then get acquainted with the properties of these general classes. For example, before we study the particular compound water, we should know a good deal about liquids in general. Before we study the gas oxygen, we shall do well to find out some of the properties all gases have in common. We shall understand salt or sugar much better if we first study the properties all solids have.

So in this unit we shall classify the various kinds of matter into general groups (or piles). We shall be thinking of the properties which the members of each general class of materials have in common, and of the energy that brings about changes in them. Then we shall be ready in Unit III to study individual specimens of matter, such as water or oxygen.

CHAPTER III

Matter and Its Kinds

[The Stuff the World Is Made of]

What is matter? By the word *matter*, in its broad sense, we mean all the stuff of which this earth, the sun, and the stars are made. To be a little more definite, we may say that *matter is anything that has weight or occupies space.* This takes in not only all the solid and liquid bodies we can see and touch but also the various gases, many of which are invisible, such as those that make up the air we breathe.

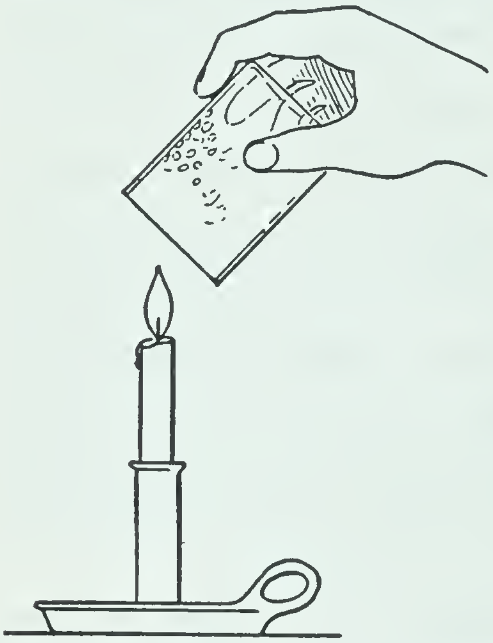

Fig. 17. This picture shows water collecting on the sides of the glass

Where does this come from ?

Can matter be destroyed? At first thought the student may say "yes" to this question. He sees the burning candle entirely disappear, the log of wood in the fireplace burn away leaving only a small fraction of its weight in ashes. What has become of this matter that has disappeared, if it has not been destroyed?

On further thought the student begins to wonder whether all the changes that take place in the burning candle can be seen by the eye — whether some invisible gases may not have been formed that escaped notice. He holds a dry drinking glass upside down just above the flame of the candle and soon discovers a film of moisture depositing on the cold sides of the glass (Fig. 17). Evidently water is produced when the candle burns, but, being in the form of steam, is invisible. He may wonder if other invisible gases have been formed, and may try to test for them. It takes the trained chemist, however, to find out everything that is happening when a candle burns or when any other chemical change takes place.

After many years of experimenting, chemists have found out that matter is neither destroyed nor created in any

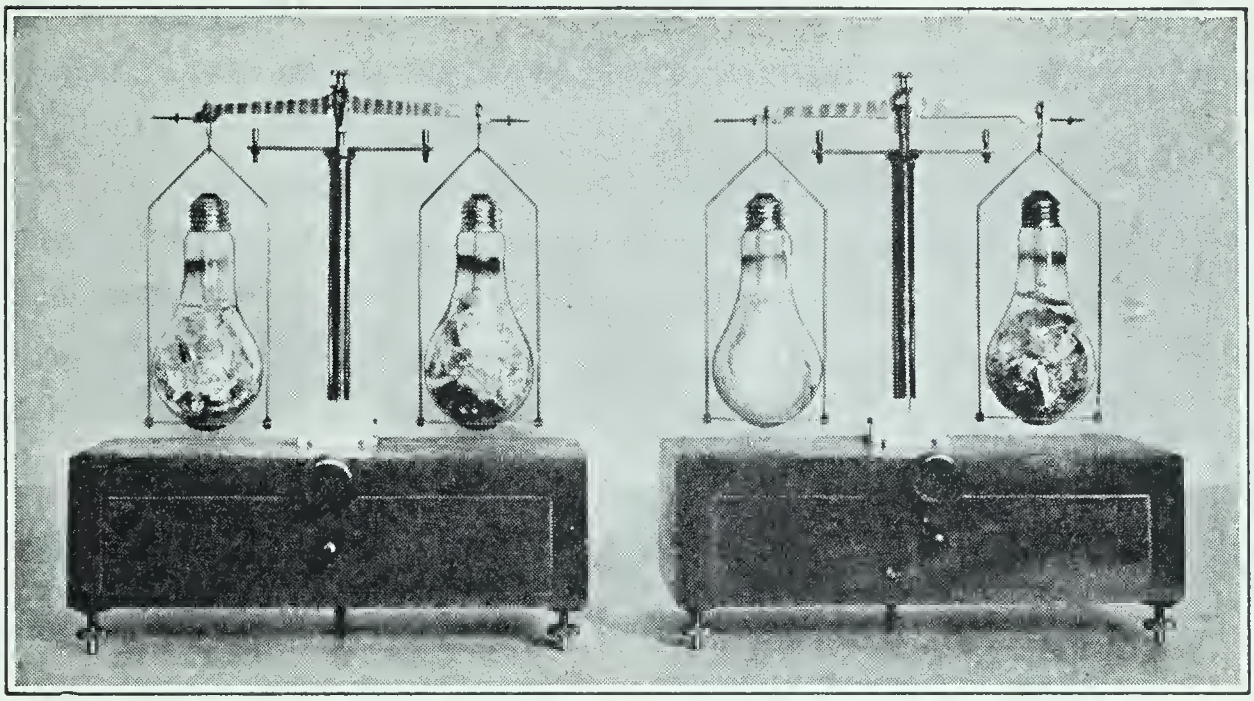

FIG. 18. Two balanced photoflash lamps before and after using one of them

The photoflash lamps used in taking flashlight pictures are filled with aluminum and oxygen. *A* shows two of these exactly balanced on the scales. One of them was ignited by a battery. The aluminum and oxygen combined, evolving much heat and light. After the lamp cooled, the two lamps again exactly balanced each other (*B*). What does the experiment show?

chemical change. If we weigh everything we start with, and then weigh everything that is formed, the two weights are exactly the same (Fig. 18). We state this fact briefly as

The law of conservation of matter: Matter is neither created nor destroyed in any chemical change.

Ways of classifying matter. We all realize that there is no limit to the kinds of objects in the world. To go very far in their study, we must arrange them in convenient groups, or *classify* them. For example, we may classify men by their nationality or their business or professions; or pupils in your class as boys and girls, or good, fair, and poor students. In the same way we may classify matter as *solids*, *liquids*, and *gases*. Many kinds of matter are well known in all these forms. Ice, liquid water, and steam are all forms of water. The solid, the liquid, and the gaseous condition are called the *three states of matter*.

The chemist, however, is not interested so much in the state of matter as he is in its *composition*. So he divides matter according to its composition into three classes. These he names (1) elements, (2) compounds, and (3) mixtures.

Elements, the building blocks of matter. We have seen in Chapter I that the modern idea of an element is that it is one of the building blocks of matter. It took many years of experiments for chemists to find out how many of these elements there are and whether they could be sure they had found them all. But now it is agreed that there are only ninety-two elements in nature.

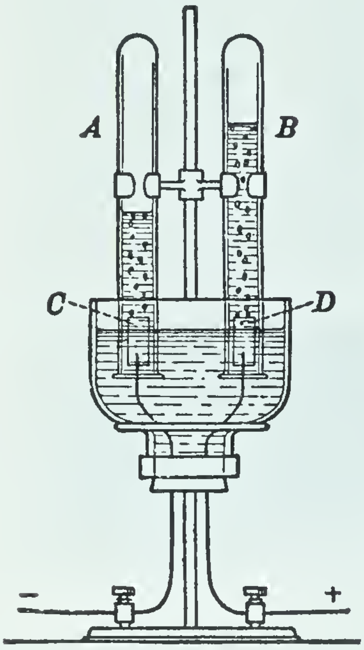

Fig. 19. Decomposition of water

When the wires shown in the figure are connected with a battery, the water in the vessel is decomposed into hydrogen, which escapes at *C* and collects in tube *A*, and oxygen, which escapes at *D* and collects in tube *B*. For details see Fig. 55

An element is one of the ninety-two building blocks of which all material things are made.

All these elements are thought to be known, although some chemists have doubts in regard to two or three of them. Many of them are familiar to all of us, such as iron, gold, silver, copper, sulfur, and oxygen. At ordinary temperatures most of the elements are solids, ten are gases, and only two, mercury and bromine, are liquids. A list of the elements is printed on the inside of the back cover of this book. We shall become familiar with the most important of these as we go on with our study.

Compounds, the union of elements. While there are only ninety-two elements, there are hundreds of thousands of substances made up of two or more elements. Water was long thought to be an element, but later it was found that an electric current decomposes it into two invisible gases, called oxygen and hydrogen, each of which is a true element (Fig. 19). The sugar that sweetens our food is composed of the three elements carbon, oxygen, and hydrogen. All substances, such as water and sugar, that are made up of the union of two or more elements are called *compounds*.

Each pure compound has a perfectly definite composition by weight. Water, for example, always contains oxygen and hydrogen in the proportion of 1 part by weight of hydrogen to exactly 7.94 parts by weight of oxygen, or 11.19 per cent of hydrogen and 88.81 per cent of oxygen — never more and never less. It makes no difference from what source we get the water — by melting ice or condensing steam, or from rivers or wells or the ocean; it has exactly this composition *provided it is pure water.* In a similar way, pure sugar always has the following composition, no matter what the source of the sugar may be: carbon, 42.08 per cent; hydrogen, 6.48 per cent; oxygen, 51.44 per cent — never more or less than these percentages. So we may make the following definition of a compound:

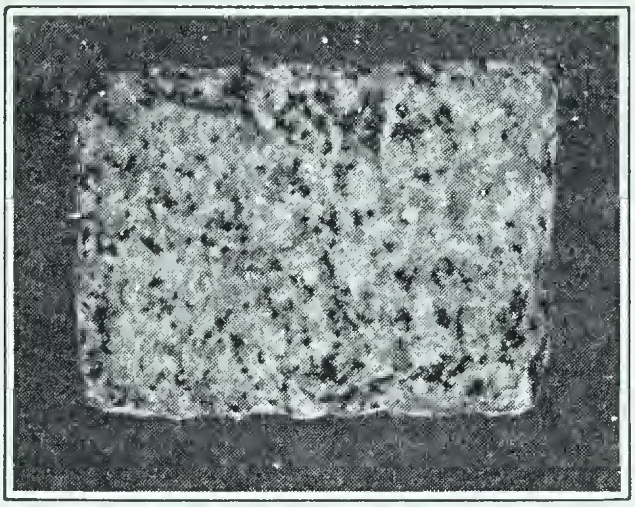

Fig. 20. A picture of granite. Is this rock an element, a compound, or a mixture?

A compound is a substance made up of the union of two or more elements in definite proportions by weight.

Mixtures, the form in which most common materials are found. Most of the materials found in nature or made in factories are neither pure elements nor compounds but *mixtures* of them. They have no fixed composition. We can easily see that many coarse-grained rocks, like granite, are made up of two or three distinct materials (Fig. 20). Concrete is made by mixing stone, cement, and sand in variable proportions. Air is a mixture of gases, chiefly oxygen and nitrogen. We can mix salt with sugar or sand or water in any proportion we like.

Illustration. The printed matter on this page illustrates very well the distinction we make between elements, compounds, and mixtures. The various letters correspond to the elements. There are not many of them, but they can be put together in many combinations to make words. The words correspond to compounds. Just as there are many more words than letters, so there are many more compounds than elements. Each word has a definite number of letters in it and is always spelled in the same way, or has a definite percentage composition of letters. Both separate letters and words can be mixed in all sorts of ways to make up a great variety of sentences, corresponding to mixtures of elements, of compounds, or of both.

Substances. There are many things we often want to speak of without saying whether they are elements, compounds, or mixtures. This is true of such things as paper, rubber, glass, clay, iron, salt. All of these are easily described and are more or less uniform in appearance. We call such things *substances*, which implies nothing about their composition. An automobile would not be a substance, for it has many parts; and we call it an object. The gasoline it burns *is* a substance, well marked in its appearance and in many other characteristics. To call it a substance does not say that it is either an element, a compound, or a mixture.

Appearances are not to be trusted. You might think that a trained chemist, knowing just what the different elements look like, could tell what elements are present in a compound by merely looking at it. This is not the case. Appearances are deceptive in chemistry as in many other things, and nature is fond of giving us puzzles. Who would think in looking at it that water is made up of two invisible gases? Who would suppose that heating sugar could decompose it into water and black charcoal? The mineral called "fool's gold" is a compound of iron and sulfur. It looks like gold but is not, as more than one person has found out to his sorrow.

One can tell little or nothing about the properties of a compound from the properties of the elements that compose it. Hydrogen burns in oxygen with a hot flame; yet water, formed by their union, is the common fire extinguisher. Neither hydrogen, nitrogen, nor carbon is poisonous; yet combined in certain proportions they form prussic acid, one of the most poisonous compounds known, a single drop of it causing almost instant death.

Chemical affinity, or the thing that makes chemical actions go. When we see small pieces of iron, such as filings, attracted to a magnet, we say some force is acting on the iron to set it in motion toward the magnet and hold it there. We give a name to this force and call it magnetic attraction or magnetism. We notice that all objects free to move fall toward the earth. We argue that there must be some force that pulls them there and holds them at the earth's surface, and we call it *gravity.*

We argue in an entirely similar way about chemical action. There must be some force that draws elements into combinations with each other to form compounds and holds them in chemical combination. This force is electrical in nature, and we call it *chemical affinity.* Scientists have long recognized the existence of these forces, but only within recent years have we begun to get some idea about their nature. We shall learn more about chemical affinity in a later chapter.

Chemical affinity is the force that causes elements to unite and holds them in combination with each other.

The relative abundance of the elements. It would be natural to suppose that all the elements are to be found on the earth in nearly equal quantities. But everyone knows that gold and silver are hard to find, while iron is very abundant. An even greater difference is true of the occurrence of other elements. Oxygen makes up nearly half the weight of all that part of the world we know much about — the air, the water, the surface rocks, and all living things. Silicon, one of the elements in sand and most rocks, makes up about one fourth of the solid earth as we know it. These two elements together compose three fourths of the world known to us. Of the other ninety elements some are relatively abundant, while others are so rare that less than 1 gram has ever been obtained. We can hardly help wondering why this great unevenness should be.

From the analysis of all sorts of rocks the late F. W. Clarke, of the United States Geological Survey, made the following estimate of the abundance of the elements in the solid 10-mile-deep part of the earth's crust:

COMPOSITION OF THE EARTH'S CRUST

	PER CENT		PER CENT
Oxygen	46.71	Sodium	2.75
Silicon	27.69	Potassium	2.58
Aluminum	8.07	Magnesium	2.08
Iron	5.05	Hydrogen	0.14
Calcium	3.65	Other elements	1.28

The very great number of compounds. Probably half a million definite compounds are known, and each year many more are added to the list. Fortunately, a fairly good understanding of a small number of these is enough to give a student a working knowledge of chemistry. It is much more important to grasp the *principles* of a science than to master a great many details. There are millions of people in the United States, but one does not need to know them all to understand the fundamental problems of our national life.

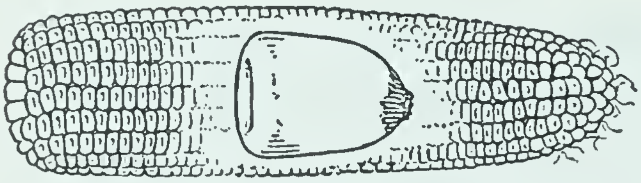

Fig. 21. Elements in a kernel of corn

Each kernel of corn has this composition: oxygen, 46 per cent; carbon, 45 per cent; hydrogen, 6 per cent; nitrogen, 2 per cent; mineral matter, 1 per cent

What elements are essential for life? It is a surprising fact that living things, both plant and animal, require few elements for their body structures. About 99 per cent of a kernel of corn (Fig. 21) is made up of the four elements carbon, oxygen, hydrogen, and nitrogen. About 96 per cent of the human body (see table) is composed of these same elements. Yet apparently the remaining 4 per cent is of great importance. We could not live a day without our minute percentage of iron; and some diseases are due to the lack of similar percentages of various elements.

AVERAGE COMPOSITION OF THE HUMAN BODY

	PER CENT		PER CENT
Oxygen	65.00	Chlorine	0.15
Carbon	18.00	Magnesium	0.05
Hydrogen	10.00	Iron	0.004
Nitrogen	3.00	Manganese	0.0003
Calcium	1.50	Iodine	0.00004
Phosphorus	1.00	Fluorine, copper, zinc, silicon, and some other elements	traces
Potassium	0.35		
Sulfur	0.25		
Sodium	0.15		

In what form are elements found in nature? Most of the elements are found in the form of compounds (united with other elements), or, as we say, in the *combined* condition. For example, iron is usually found combined with oxygen or

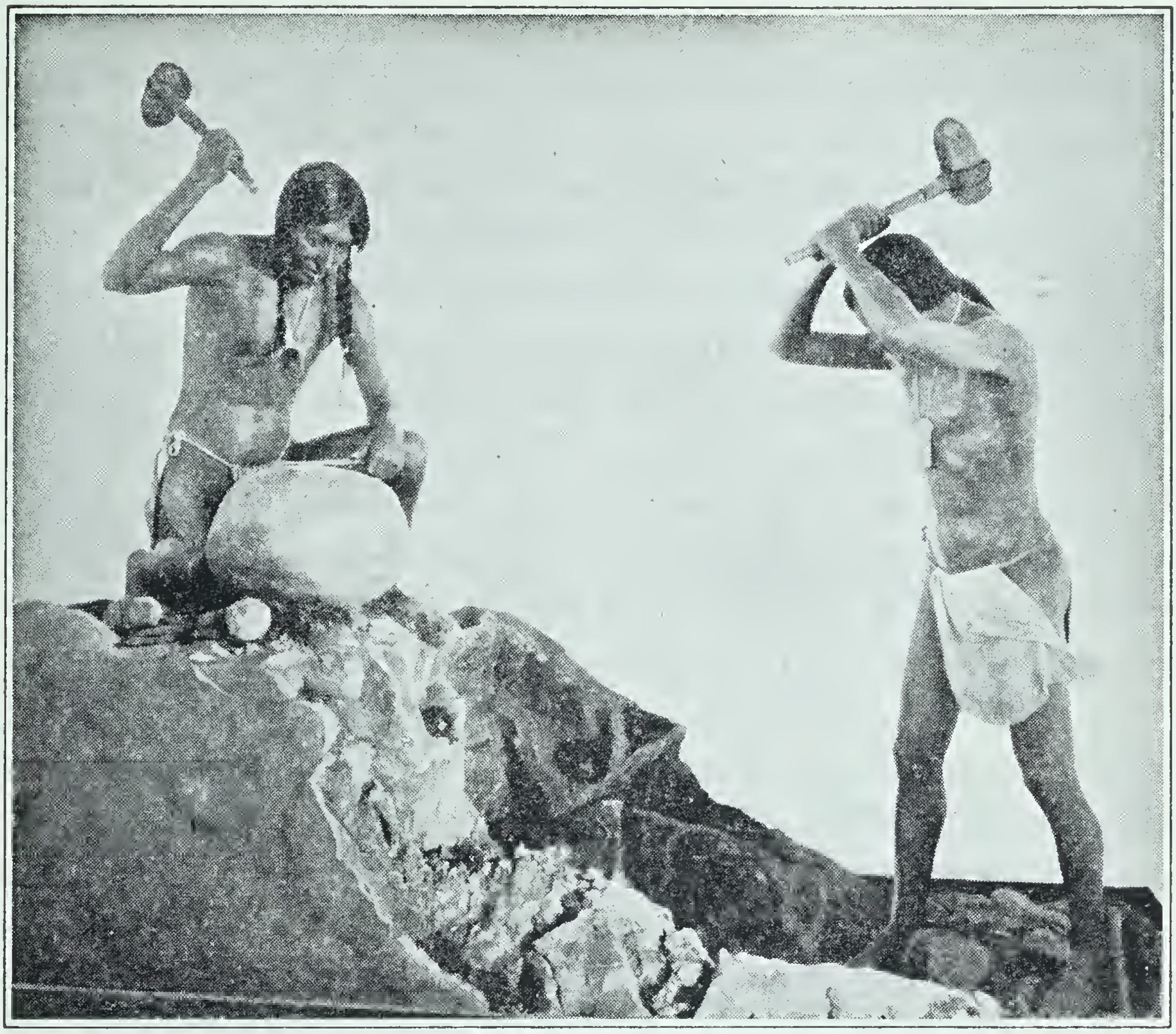

Fig. 22. The early natives mining copper. Why was copper used so early in the history of our race?

By courtesy of the United States National Museum

with sulfur. The elements that make up our bodies are all in the form of compounds, of which water is the most abundant.

A few of the elements are sometimes found in nature uncombined with another element, and we then say they occur in the *free* state, or *native.* Among these are gold, copper (Fig. 22), oxygen, and sulfur.

How the elements were named. Whoever discovers an element gives it its name, just as he names his own child. So names have been given for all sorts of reasons. Some names, like *gold* and *iron*, are so old that we are not sure of their original meaning, nor even of the languages from which they came. Many names were suggested by some striking property of the new element. For example, *phosphorus* means "light-bringer," or "light-carrier"; *chlorine* means "greenish-yellow." Some chemists have been very patriotic and have given their country's name to their chemical child. So we have *scandium*, *germanium*, *gallium* (France), and *illinium* (Illinois). Other chemists have romantically chosen names from gods and heroes of old; as, *thorium* and *tantalum.*

Symbols, the short names of elements. Just as we indicate the names of states by abbreviations, such as O., Va., and Mo., so the chemist shortens the names of the elements and calls the short form a *symbol.* Sometimes the symbol is merely the first letter of the full name; as, O for oxygen, C for carbon, N for nitrogen. Usually it is necessary to add a second letter to the symbol, because several names begin with the same letter. C is the symbol for carbon, Ca for calcium, Cl for chlorine, Cd for cadmium. Some symbols come from the old Latin name of the element: Fe (*ferrum*) stands for iron, Cu (*cuprum*) for copper, and Hg (*hydrargyrum*) for mercury. The symbols for all the elements are listed on the inside of the back cover of this book.

The symbol and the atom. We have seen that the Greeks got the idea of the atom by speculation. Today we have reached this idea by experiments, which will be described in a later chapter; but we may state here a little of what we shall prove later on. We know by *experiment* that any given weight of an element, such as a gram of iron, is made up of a vast number of tiny particles called *atoms.* A load of very clean sand is also made up of nearly uniform grains, but a grain of sand is many thousands of times larger than any atom.

Now the chemist finds it convenient to let the symbol of an element stand not only for the *element* but also for a definite amount of it, namely, one *atom.* H stands for one atom of hydrogen, O for one atom of oxygen, and Hg for one atom of mercury.

How the chemist uses the symbols. Since every compound is made up of at least two elements, it must be made up of at least two kinds of atoms, each having its own symbol. So the chemist has devised a sort of chemical shorthand. He uses the symbols of the atoms to show the composition of a compound instead of spelling out the full name. For example, the red, solid compound called mercuric oxide is formed by the union of mercury and oxygen; that is to say, by the union of mercury atoms with oxygen atoms. In addition the chemist has found that these two kinds of atoms that make up mercuric oxide are present in equal numbers. So in chemical shorthand the name *mercuric oxide* is written HgO. This means simply a compound of mercury and oxygen with atoms of each in equal numbers — one to one. The shorthand name of mercuric oxide, HgO, is called its *formula.*

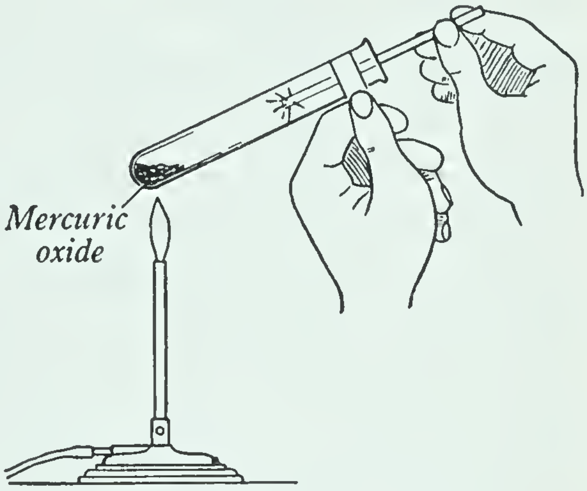

Fig. 23. Heating mercuric oxide in a tube

What causes the glowing spark to burst into flame?

How the chemist represents a chemical change. A chemical change may be represented briefly by the use of symbols and formulas. If we heat some mercuric oxide in a test tube (Fig. 23), we find that the compound is decomposed into mercury and oxygen. The mercury collects on the sides of the tube in the form of a silverlike liquid which we recognize as the "quicksilver" used in thermometers and barometers. The oxygen escapes as an invisible gas, which will cause a glowing spark, on the end of a splinter of wood, to burst into flame (Fig. 23). The chemist represents this decomposition of mercuric oxide into mercury and oxygen by an *equation* using his formulas and symbols, as follows:

$$\mathrm{HgO} \longrightarrow \mathrm{Hg} + \mathrm{O}$$

He uses an arrow (⟶) rather than the equation mark (=) so as to show what he starts with and what is formed.

Atoms and molecules. Now, as we shall see later on, the chemist has found out some strange things about mercury and oxygen. The atoms that make up mercury, like the atoms of most other metals, stay as single atoms. But as fast as the oxygen atoms are set free from the mercuric oxide, *they unite with each other in pairs*, and we call each pair a *molecule.* So the chemist makes this distinction: The individual particles of an element he calls *atoms.* The particles made up of two or more atoms, whether they are atoms of different elements or of the same element, he calls *molecules.*

More about equations. Just as the symbol of an element represents 1 *atom* of the element, the formula of a compound represents 1 *molecule*. If we wish to indicate, say, two molecules, we write the number 2 before the formula; thus, 2 HgO. Since the oxygen molecule is a combination of two atoms, we might write it OO. But the chemist finds it much more convenient to write it O_2, in which the subscript $_2$ shows the number of oxygen atoms in the oxygen molecule. There is a difference, then, between 2 O and O_2. The former represents two atoms of oxygen uncombined, while the latter represents the two atoms combined in the form of a molecule. In order to express these additional facts, we now rewrite the equation

$$HgO \longrightarrow Hg + O$$

in the following form:

$$2\ HgO \longrightarrow 2\ Hg + O_2$$

While both these equations tell us that mercuric oxide decomposes into mercury and oxygen, the latter is the better one, because it gives us the additional information that the mercury atoms set free remain free, while the oxygen atoms unite to form molecules of oxygen. It is evident that in these equations, as well as in all others representing chemical changes, there must be just as many atoms of each element on one side of the equation mark ($\longrightarrow$) as on the other. Otherwise the equation would indicate that matter had been either created or destroyed; and this is not possible.

The formula for water. By experiment the chemist has found that water is made up of oxygen and hydrogen, and that the water *molecule* consists of two atoms of hydrogen and one of oxygen. These facts are expressed in the formula for water, H_2O. The subscript $_2$ refers to the symbol that it follows. This is the same as though it were spelled out H-two O.

Later on we shall see how the chemist finds out how many of each kind of atoms there are in the molecule of a given chemical compound. We shall also see that he puts many more facts into these shorthand formulas and equations than have been explained here. At present we shall use them in the way we have explained.

Physical properties and chemical conduct. In getting acquainted with any given element or compound, we want to know two kinds of things about it: (1) what it is like, or its *physical properties*; (2) how it acts chemically toward other things, or its *chemical conduct.*

Physical properties — what a thing is like. To answer this question we must first use our five senses. By these we can tell its physical state (solid, liquid, gas), its color, odor, taste, luster, transparency, solubility. We can then make all sorts of measurements, finding its melting point, boiling point, density, hardness, electrical conductance, and any other measurable qualities by which we can describe it. All these are *physical properties.*

Chemical conduct — how a thing acts. The conduct of a person is how he acts toward other people — his social behavior under a variety of circumstances. The chemical conduct of an element or of a compound is how it acts toward other substances; how it is affected by heat, or electrical currents, or sunlight; in general, how it *behaves*, or acts, chemically. This is of great importance; for, as the famous English scientist Faraday said, nearly one hundred years ago, "It is not the best-looking thing but the best-acting thing which is the most advantageous to us." And this is true of human beings as well as of elements and compounds.

Energy. So far we have pictured the chemist as interested in *matter.* He is equally interested in that other great side of nature called *energy.* Every one of you knows that when coal burns heat is given off, and that power lines carry an electric current. You know also that by the use of a steam engine and an electric motor both the heat and the electrical current can be made *to do work.* Now anything that can do work is said to have energy, and we may define energy as follows:

Energy is the ability to do work.

Heat, electrical current, light, the movement of bodies, magnetic attraction, are forms of energy.

Chemical energy. A body may have energy because of its motion, as in the case of falling water that is made to run a dynamo and generate electricity. Or it may possess energy

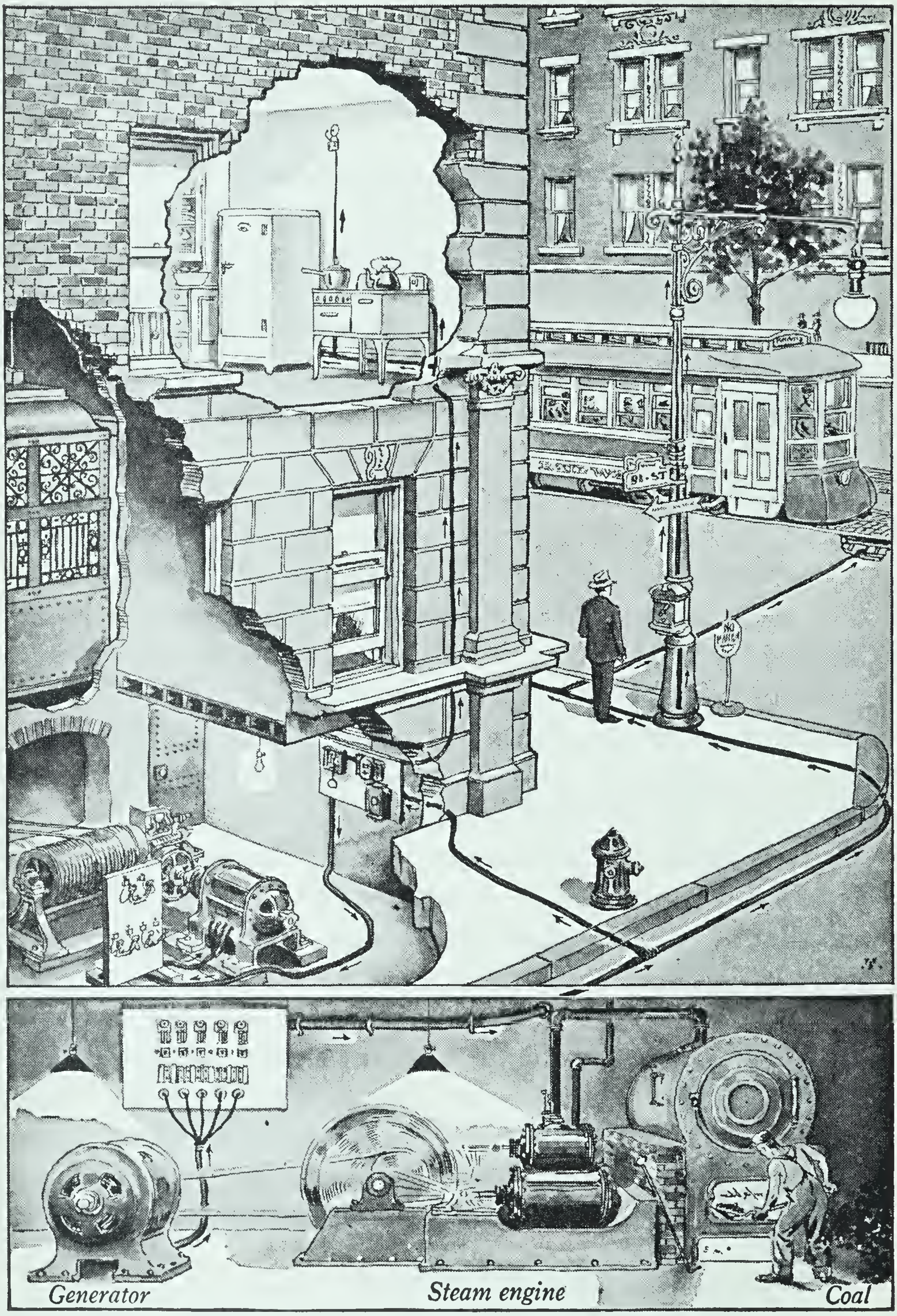
91-ST
NO PARKING
Generator
Steam engine
Coal

FIG. 24. Transformations of energy

Starting with the energy in the coal used in firing the engines, trace the transformations of energy shown in the picture due to its position, as when we hoist a heavy weight and allow it to drop on a pile and so drive the pile into the ground. Finally, a body may possess energy because it can undergo chemical change. This form of energy we call *chemical energy,* and it is the form in which the chemist is most vitally interested. For example, all fuels possess chemical energy. When the fuels are burned, the chemical energy is transformed into other forms of energy, especially heat, which may be made to do all sorts of work, such as moving a train of cars or flying an airplane. An ordinary storage battery is simply a device for transforming the chemical energy of certain materials into electrical energy. Explosives consist of various materials that possess enormous chemical energy.

The law of conservation of energy. We have already seen that matter can be neither created nor destroyed, and this fact is expressed in the law of conservation of matter (p. 25). Likewise, all our experiments go to prove that *energy can be neither created nor destroyed.*

Law of conservation of energy: Energy can be neither created nor destroyed.

What, at first thought, may seem to be the creation of energy is really the result of changing one kind of energy to another. Indeed, most of our machines are simply devices for transforming one kind of energy into another better suited to our needs (Fig. 24).

CHAPTER SUMMARY IN QUESTION FORM

1. "The world is made up of matter." What is meant by the word *matter* in this sentence?

2. (*a*) What is the name of the law that expresses our belief regarding the creation and destruction of matter? (*b*) State the law.

3. (*a*) Give two ways in which we may classify matter. (*b*) In which of these is the chemist more interested?

4. (*a*) What is an element? (*b*) Chemists believe in the existence of how many elements in nature? (*c*) How many of these are known?

5. (*a*) Name two characteristics of compounds. (*b*) How many compounds are known?

6. How do mixtures differ from elements and compounds?

7. (*a*) Can you tell by its appearance what elements are in a compound? (*b*) Give an example to illustrate your answer.

8. (*a*) Can you tell the properties of a compound from the properties of the elements present in the compound? (*b*) Give examples to illustrate your answer.

9. What do we call the force that causes elements to unite to form compounds?

10. Name two elements that together make up about three fourths of the earth's crust.

11. (*a*) Name three elements that constitute over 90 per cent of our bodies. (*b*) Name three that constitute less than 0.1 per cent.

12. Gold occurs in nature in a *free state*; iron, in a *combined state.* Explain the meaning of this statement.

13. Give, and illustrate by examples, three ways in which elements have received their names.

14. (*a*) What is the symbol of an element? (*b*) How are symbols chosen? (*c*) Give examples to illustrate.

15. (*a*) What is the difference between a symbol and a formula? (*b*) Show by an example how the chemist expresses a chemical change by the use of symbols and formulas.

16. What is the difference between an atom and a molecule?

17. What questions are to be answered under the headings (*a*) "Physical properties of an element" and (*b*) "Chemical conduct of an element"?

18. (*a*) What is the difference between matter and energy? (*b*) Name different forms of energy. (*c*) What kind of energy does a storage battery possess?

19. (*a*) In what respect are matter and energy alike? (*b*) State the law of each that expresses this similarity.

THOUGHT QUESTIONS

1. Explain the phrase "definite percentage composition."

2. Air is composed largely of a mixture of oxygen and nitrogen. Suppose it were a compound of these two elements: in what respects do you think it might differ from the mixture?

3. Suppose a certain substance is not changed on heating. Does this prove the substance to be an element?

4. Select from the words in column *A* the one (or ones) that most accurately describe each of the words under *B*.

A	*B*	
Element	Water	Lead
Compound	Sugar	Salt
Mixture	Grapefruit	Gold
Substance	Coffee	Butter
None of the above	Cream	Copper

5. We say that matter cannot be destroyed, but we also say that a candle burns up. Can you account for its disappearance?

6. Account for the fact that the ancients were familiar with gold but not with aluminum, which is far more abundant.

7. Compare the relative quantities of iron and silicon in the earth's crust. How do you account for the fact that everyone is familiar with iron and but very few with silicon?

8. What form of energy is used to bring about the chemical change that takes place in (*a*) the lighting of a match? (*b*) the taking of a photograph? (*c*) the charging of a storage battery?

9. State some transformations of energy that take place in (*a*) the running of an automobile; (*b*) the riding of a bicycle.

10. The energy of the falling water at Niagara Falls is used for propelling, heating, and lighting the streetcars in Buffalo. Describe the transformations of energy involved.

11. Is there such a thing as (*a*) an atom of oxygen? (*b*) a molecule of oxygen? (*c*) an atom of water? (*d*) a molecule of water? (*e*) an atom of air? (*f*) a molecule of air?

12. Draw a circle to represent the earth. Then, by drawing radii, represent the percentage of the earth composed of each of the more abundant elements present.

OPTIONAL EXERCISES

1. Weigh out a piece of fine iron wire equal to the weight of iron in your body. Does the fact that the percentage of iron in the body is so small mean that it is unnecessary for health?

2. Give the source of (*a*) the heat in your body; (*b*) the heat of an electric light; (*c*) the heat given off by a burning candle; (*d*) the heat generated in pumping air into an automobile tire; (*e*) the heat generated by sawing a piece of hard wood.

3. Consult the dictionary for the derivation and meaning of the following names of elements: (*a*) phosphorus, (*b*) hydrogen, (*c*) germanium, (*d*) columbium, (*e*) chlorine, (*f*) argon, (*g*) copper, (*h*) selenium, (*i*) thorium, (*j*) tantalum.

CHAPTER IV

States of Matter

[Matter: a Thing of Three States but Many Kinds]

The three states of matter. In Chapter III we defined matter as anything that has weight or occupies space. We also called attention to the fact that while matter may take on a great many different shapes and appearances, it may all be grouped under three heads — namely, solids, liquids, and gases — and that these are known as the three states of matter.

Most of the things with which we are familiar are solids. A few, especially water, are liquids. Some are mixtures of these two, as is true of the food we eat. We are not so familiar with gases, because most of them are colorless and so we cannot see them. None of the common ones that make up our atmosphere has an odor. Strange to say, we are living at the bottom of a deep ocean of gases; yet we rarely realize this unless a strong wind is blowing. In olden times air was the only gas known, and was thought to have no weight and not to be matter of any kind. There was much mystery about it. Today we are acquainted with many gases, and know that they represent simply one of the states of matter.

The state of a pure substance not fixed. One might suppose that any given pure substance, like salt or oxygen, would be found in one definite state: that salt would always be solid, and oxygen always gaseous. This is not so. We all know that pure liquid water can be frozen into a solid (ice) or boiled into a gas (steam). Liquid air (Fig. 25) is sold every day, like gasoline, by the gallon, and the gas carbon dioxide, which we exhale from our lungs, can be purchased on the market in the form of a white solid called by the trade name of *dry ice* (Fig. 26). Many pure substances can be had in any one of the three states.

How we measure a definite quantity of matter. Solids are easy to weigh; so we measure a definite quantity of a solid by weighing it. We order a *ton* of coal or sell a *pound* of butter. Liquids also are easy to weigh; but we have to make

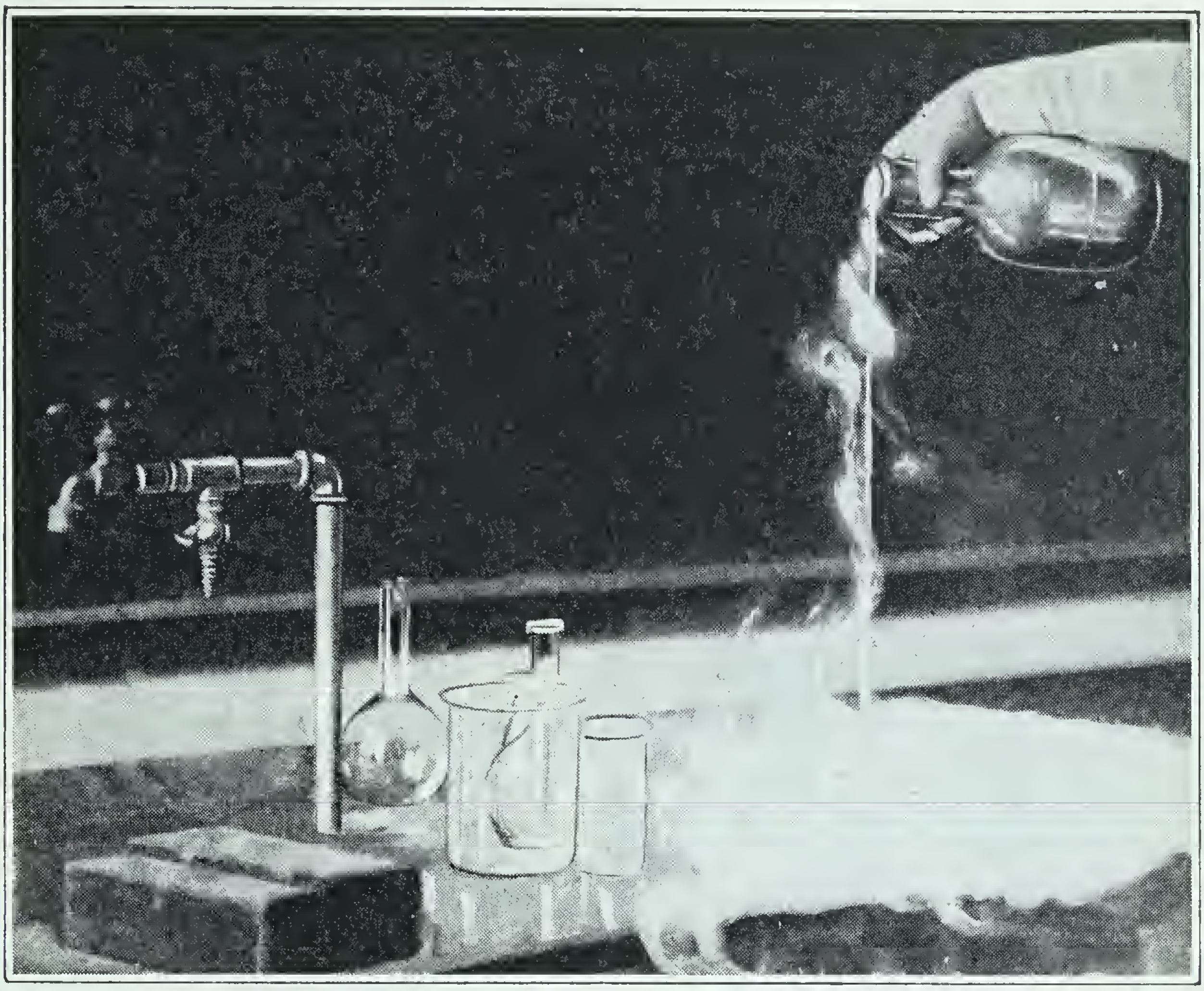

FIG. 25. Pouring liquid air from a thermos bottle

two weighings: first the empty container and then the container with the liquid in it. So instead of weighing liquids it is simpler to state the *volume*, as measured by some convenient measuring vessel. We buy gasoline by the *gallon*, and milk by the *quart*.

To weigh a quantity of gas requires a fine balance and much skill, and so we measure gases, like liquids, by the volume. Our monthly gas bill tells us that we owe the gas company for so many *cubic feet* of gas. If we wish to know the weight as well as the volume of the gas, then we must take into account the pressure and the temperature under which the gas is measured; for each of these affects the volume. It is important for us to know just how much the volume of a gas is changed by temperature and pressure; and we will now study this.

The volume of a gas is changed by pressure: Boyle's law. Everyone who has pumped up an automobile tire knows that a large quantity of air can be compressed into a relatively small space. He knows also that the more air is pumped in, the higher the pressure gauge reads. The weight of, say, a cubic inch of air in the tire increases with every stroke of the pump.

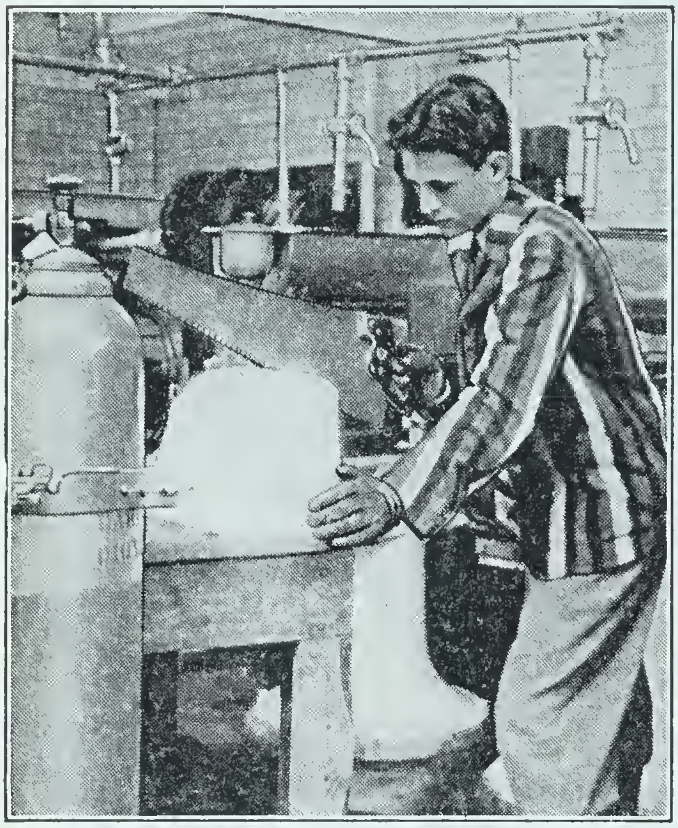

Fig. 26. Sawing a block of solid carbon dioxide into slabs for packing ice cream

Now to what extent does the volume of a gas change with the pressure? This question can be answered by careful experiments. These experiments were first carried out by the great English scientist Robert Boyle (Fig. 27). In 1660 he summed up the results of his experiments in the following statement, now known as Boyle's law:

BOYLE'S *Law: The volume occupied by a given weight of gas varies inversely with the pressure, provided that the temperature of the gas is kept from changing.*

For example, suppose we measure 1000 ml of a gas under any definite pressure we may choose. If now we double the pressure, the gas will occupy only 500 ml. If the pressure is diminished one-half, the gas will have a volume of 2000 ml (Fig. 28). It is a striking fact that all gases act in the same way, so that Boyle's law, within limits, holds good for all gases.

The volume of a gas changes with its temperature. Charles's law. The volume of a gas varies not only with the pressure put on it but also with its temperature. "Heated air expands" is a well-known saying, and this holds good for all gases. On a hot day we may sometimes see the air quivering over a heated pavement. The air in contact with the pavement is heated, expands, and streams upward through the cooler and heavier air.

About the beginning of the last century several scientists made experiments to find out the extent to which the volume of a gas is changed by changing its temperature. The results of these experiments are summed up in the brief statement known as Charles's law:

CHARLES'S *Law: If we measure the volume of a gas at 0°, and then change its temperature, keeping the pressure constant, the volume of the gas increases* $\frac{1}{273}$ *of its volume at 0° for every degree the temperature is raised, and decreases by* $\frac{1}{273}$ *for every degree the temperature is lowered.*

FIG. 27. Robert Boyle (1627–1691)

The first to define an element and to show that a compound is made up of two or more kinds of elements. Chiefly remembered for experiments with gases

For example, if a gas has a volume of 1000 ml at 0°, its volume at 1° would be $1000 + (1000 \times \frac{1}{273})$, or 1003.6, ml. At 10° it would have a volume of $1000 + (1000 \times \frac{10}{273})$, or 1036, ml. At 273° its volume would be $1000 + (1000 \times \frac{273}{273})$, or 2000, ml. If the temperature is lowered below zero, the volume of the gas is *decreased* in the same proportion. At −10° its volume would be $1000 - (1000 \times \frac{10}{273})$, or 964, ml. According to this rate, at 273° below zero the volume of the gas would be $1000 - (1000 \times \frac{273}{273})$, or 0, ml. In other words, it would be nothing. Of course, this cannot happen. Experiments show that before this temperature is reached all gases have changed into the liquid or solid state, and Charles's law does not apply to these states.

Absolute zero; absolute scale of temperature. The temperature 273° below zero, referred to in the preceding paragraph, is called *absolute zero.* It is the temperature of greatest cold. A thermometer scale with the zero mark at − 273° centigrade and with each degree equal to a degree on the centigrade scale is called the *absolute scale* of temperature. (See Appendix C.)

Pressure and temperature act on the volume of a gas in opposite directions. Increase in pressure lessens the volume of a gas; increase in temperature increases the volume. Both these effects come into play when a gas-filled balloon rises in the air. The pressure exerted by the atmosphere upon the balloon falls off rapidly as the balloon rises, and so the gas tends to expand. But the atmosphere is colder higher up, and this has the opposite effect. The effect of the change in pressure, however, is much greater than that of the change in temperature. So a balloon ready to go up is only partially filled with gas. Then, as the balloon rises, the gas expands, and the gas bag fills (Fig. 29).

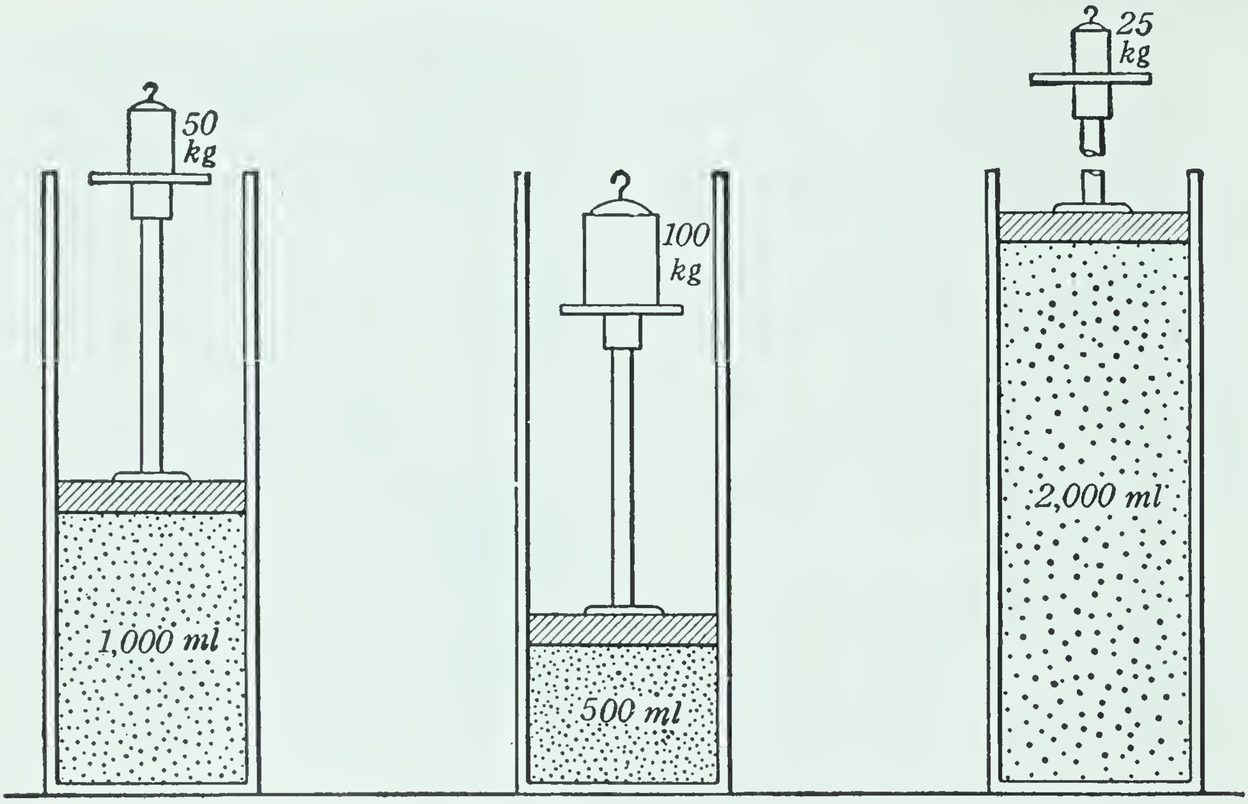

FIG. 28. Show how this figure illustrates Boyle's law

Combined changes in pressure and temperature. Since we know how changes in pressure and temperature, taken separately, affect the volume of a gas, we can find their combined effect by a simple calculation. The method for doing this is given in detail in Appendix C, for the benefit of those who may wish to use it.

Standard conditions for gases. Facing the back cover of this book is a table that gives the weight of 1 liter of each of the common gases. This table is very useful. If we are given the *volume* of any one of these gases, we can immediately turn to the table and figure out the *weight* of this volume. If we are given the *weight* of the gas, we can calculate its volume.

But since the volume of a gas changes with both pressure and temperature, the statement in the table that 1 liter of oxygen weighs 1.4290 g really has no meaning unless we are told at what temperature and pressure the gas was weighed. So chemists have agreed upon what are called *standard conditions* of temperature and pressure. These are 0° for *temperature*, and a *pressure* equal to the average pressure of the atmosphere at sea level. This is equal to a weight of 1033 g per square centimeter. So when we say that 1 liter of oxygen weighs 1.4290 g, we mean that the amount of oxygen which has a volume of 1 liter when measured at 0° under a pressure of 1033 g per square centimeter weighs 1.4290 g.

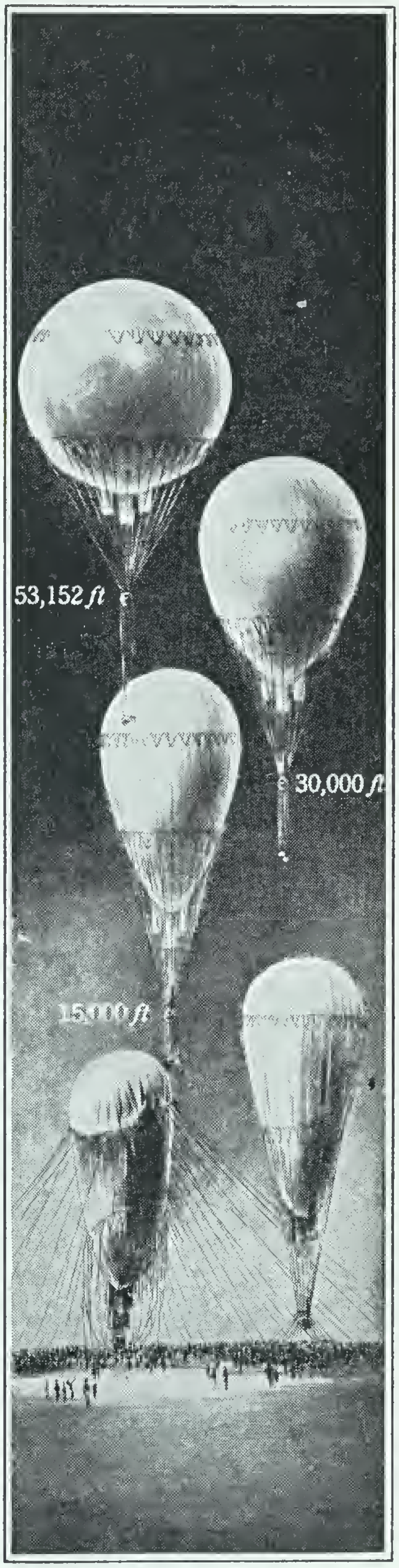

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Fig. 29. The balloon expands as it rises. Why?

Pressure as measured by barometer reading. In place of using actual weights for the atmospheric pressure, it is much more convenient in making calculations to use the barometer reading at which the gas is measured. For the height of the mercury column of the barometer varies directly with the atmospheric pressure, as is shown in Fig. 30. The barometer consists simply of a glass tube that is entirely filled with mercury and then inverted in a cup of mercury. The mercury in the tube falls until the weight of the mercury in the tube is exactly counterbalanced by the pressure of the atmosphere on the mercury in the open cup; for it is this pressure that holds the mercury up in the tube. The average normal pressure of the atmosphere at the sea level (1033 g/cm^2) will hold the mercury in the tube at a height of 760 mm. If the pressure becomes less, the mercury column falls; if it becomes greater, the mercury column rises.

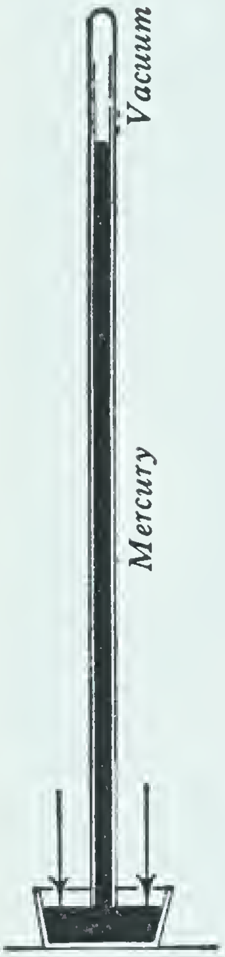

FIG. 30. A simple barometer

Heat changes that go along with volume changes in gases. In the days when we had to pump up automobile tires with a hand pump, everyone knew that the pump got hot. This was not due to friction in the pump, but to heat that is always set free when a gas is compressed. So, too, when we open the valve in a tire, we can feel that both the casing and the escaping air are being *cooled*. *Heat is always liberated when a gas is compressed, and is absorbed when a gas expands.* Later on we shall see that these heat changes are of great importance in the process of liquefying various gases.

Summary of facts about gases. We have now learned a number of *facts* about gases: (1) They exert a pressure on the walls of any vessel in which they are confined. (2) They tend to expand until they fill evenly any vessel in which they are confined. (3) They contract when the pressure on them is increased, and expand when it is decreased. (4) They expand when heated and contract when cooled. How do we account for these facts? When we meet a set of facts in everyday life that awaken our curiosity, how do we reason out an explanation of them?

What is a theory? We see a man running down the street, and, at some distance behind, another man running in the same direction. We are interested in these *facts*, and we wonder if the one fact has anything to do with the other. We may *imagine* a number of explanations. Is the man ahead running away from an enemy pursuer? Is the man behind trying to catch up with his friend ahead? Are they both merely trying to catch the same train? When we imagine explanations of this kind about the *facts* of science, we call it *forming a theory*.

A theory is a guess, or an imagined picture, that makes it easier for us to understand the relation of a number of facts to each other.

The kinetic theory of gases. About a century ago scientists began to imagine a picture of the make-up of gases that would agree with the known facts. This guess, or picture, was called the *kinetic theory of gases,* the word *kinetic* meaning "due to motion." Its main points are these: (1) Every gas is made up of very minute particles called *molecules.* (2) All molecules of the same gaseous element or compound are exactly alike in their weights, while molecules of different elements or compounds have different weights. (3) The gaseous molecules are in very rapid motion, like bees in a swarm. They are constantly hitting each other and the sides of any containing vessel and rebounding, as billiard balls rebound from each other or from the cushion of the billiard table. (4) When a gas is heated, the speed of its molecules is increased.

The kinetic theory and the facts. Let us see how well this theory fits the facts we have learned about gases. (1) The molecules have weight and are moving with high speeds — much faster than a rifle bullet. Millions of them hit the sides of the containing vessel every second, and this results in a steady pressure against those sides. A sandblast directed against a wall makes a similar pressure on the wall. (2) If these fast-moving molecules were not confined in a vessel, they would fly away in all directions; that is, the gas would expand indefinitely. (3) The molecules are far apart as compared with their own size, so that when we compress a gas we simply crowd the molecules more closely together. They will then hit the sides of the vessel oftener and for this reason exert a greater pressure upon it. (4) Heat increases the speed of the molecules; consequently they will exert a greater pressure at a higher temperature. If we wish to keep the original pressure, we shall have to allow the gas to expand somewhat, in accord with Charles's law.

We now know that these guesses which made up the kinetic theory were a wonderfully accurate explanation. There is no doubt that molecules exist and that they are in violent

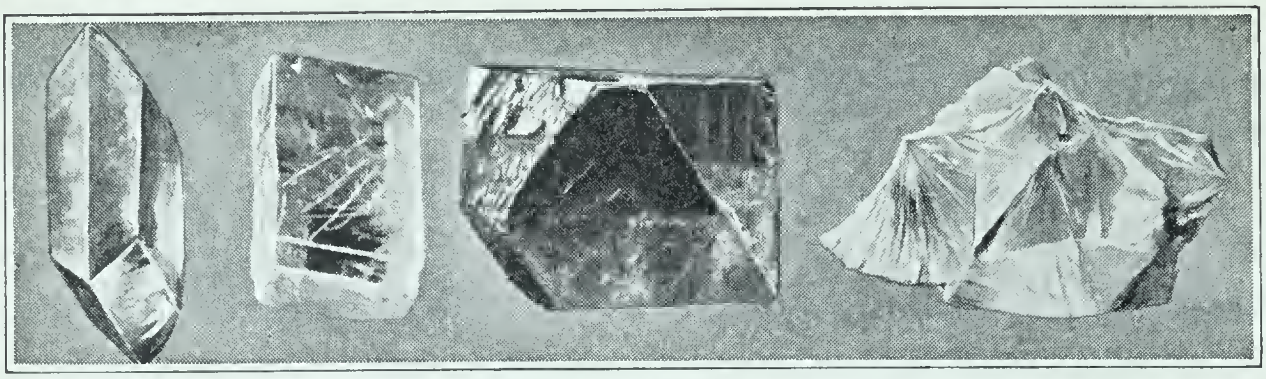

Fig. 31. Some specimens of minerals found in nature. Are they crystalline or amorphous solids?

motion. We can even calculate their number in a liter of gas with greater accuracy than we can count the number of people living in a large city. The original kinetic theory has now become accepted beyond dispute.

Of what use is a theory? As we go along in this study we shall meet with a number of theories. We have seen that a theory is an effort of the imagination to explain the cause of a number of related facts that have been found by experiment. Or it may be an effort to find the reason why things are as we find them to be. When we have made a theory, our next step is to test it in every way we can think of to see whether it fits all known facts. This testing almost always leads to the discovery of some new facts that may or may not fit the theory. If they do not fit, we either make the necessary changes in the theory or try to imagine a better one. So a theory has two very definite uses: (1) It gives us our facts *in picture form*, which makes it easy to remember them, much as a good road map is easier to follow than a lot of careful directions. (2) The testing of the theory makes us invent new experiments that often lead to new knowledge. This is much better than making experiments at random, with no particular end in view. You bag more game if you shoot *at* something than if you merely shoot.

Solids and liquids — their structure. We have seen that a gas consists of a vast number of molecules in violent motion. Suppose we condense the gas to a liquid. What happens to the molecules? Does the motion of the molecules stop? We can answer this question only by experiment, and by this means we find that the motion of the molecules continues but that they move more slowly and are very close together.

They have also considerable attraction for each other; but this attraction is not strong enough to hold the molecules in any fixed position, and so the liquid adjusts itself to the shape of the vessel that contains it.

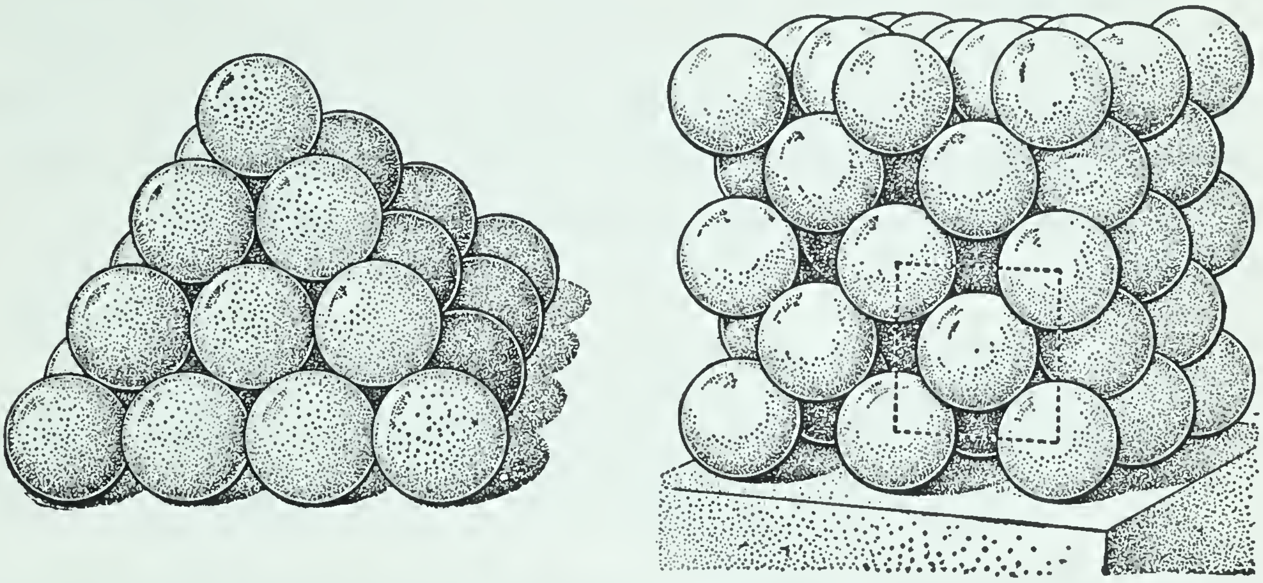

FIG. 32. These figures (highly magnified) show how the atoms (or molecules) are arranged in some crystals

In a solid the motion of the molecules is so slow that the attractive forces acting between the molecules pull them into some definite position about each other, so that a solid retains its shape unless subjected to great pressure.

Crystals. Most solids, whether elements or compounds, tend to arrange their parts in perfectly definite shapes, forming *crystals* (Fig. 31). The form of the crystal varies with the solid, but for each solid it is as definite as the melting point of the solid. These crystals vary greatly in size. Often they are so small that we can detect their crystalline form only by the aid of a microscope; less often they are very large.

Such crystalline solids, whether elements or compounds, are not made up of simple molecules, as are liquid water and gaseous carbon dioxide. Each crystal is built of atoms or groups of atoms (often electrically charged) or of molecules, systematically arranged in a definite space pattern in a sort of gigantic molecule forming the entire mass of the crystal. Fig. 32 illustrates two of the ways in which the parts of the crystal are arranged. Of course, these parts as shown in the figure are enormously magnified. They remind us of the way the grocer gets our attention by building up apples or oranges into some definite form. One may still see cannon balls piled up in this fashion in old courthouse yards.

Amorphous solids. Many solids, such as the ordinary clay of our soils, show no orderly arrangement or crystal structure of any kind. Their molecules are lumped together in huge numbers without any order. A solid made up in this way is said to be *amorphous*, which means "without form."

CHAPTER SUMMARY IN QUESTION FORM

1. Name the three states of matter, giving an example of each.

2. Give an example of a substance you know to exist in each of the three different states.

3. What are the common units, both English and metric, used in measuring weights and volumes of each of the states of matter?

4. Give two ways of changing the volume of a gas, and illustrate each with an example.

5. State Boyle's law.

6. State Charles's law.

7. (*a*) What is meant by *absolute zero*? (*b*) by *absolute scale of temperature*?

8. What are the standard conditions used in measuring the volumes of gases?

9. What is to be taken for granted when we state that 1 liter of oxygen weighs 1.429 g?

10. What heat changes take place (*a*) when air is forced into an automobile tire? (*b*) when the valve on a tire is removed, allowing the air to escape?

11. (*a*) What is a theory? (*b*) How do theories differ from facts?

12. Give the four chief points of the kinetic theory.

13. Show how the kinetic theory accounts for the properties of gases.

14. Of what use is a theory?

15. Are the molecules of the same element or compound identical or different?

16. Contrast the properties of a gas with those of a liquid and those of a solid.

17. (*a*) What name do we give to substances like sawdust, whose particles have no definite form? (*b*) What name do we give to substances like a diamond, whose particles have flat surfaces and sharp edges?

THOUGHT QUESTIONS

1. You cannot see, taste, hear, feel, or smell the air in a quiet room. How, then, can you prove that air is really a form of matter?

2. Point out a possible source of error in the following reasoning: "I filled a 500-ml flask with oxygen in the laboratory. This must weigh 0.7145 g, since the table on the inside back-cover page gives the weight of 1 liter of oxygen as 1.429 g."

3. (*a*) Does a theory ever become a fact? (*b*) Does a fact ever become a theory?

4. When air is compressed, heat is given off; when it expands, heat is absorbed. Explain where the heat comes from in the first case, and what becomes of it in the second.

5. All known gases have been liquefied and solidified. Not all solids, however, have been obtained in the gaseous and liquid states. How can you account for this?

6. (*a*) How could you prevent the expansion of a gas when it is heated? (*b*) Account for the explosion that might result.

7. Calculate the volume (*a*) of 100 g of oxygen measured under standard conditions; (*b*) of 100 g of hydrogen.

8. A certain weight of gas occupied a volume of 500 ml when the barometer read 760 mm. If the gas is free to change its volume, and the temperature remains constant, calculate the volume that the gas would occupy at each of the following barometric readings: (*a*) 740 mm; (*b*) 780 mm.

9. A certain weight of gas had a volume of 100 liters under standard conditions. Suppose the temperature were to change from 0° to 50° (pressure remaining constant): what volume would the gas then occupy?

OPTIONAL EXERCISES

1. State some important fact the explanation of which is unknown to you; then form a theory that would account for the fact.

2. Give the names of all the great chemists mentioned so far in our study, and state one important discovery by each.

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3. A gas under standard conditions measured 100 liters. Suppose its temperature were raised to 50° and at the same time the pressure upon it were doubled: what volume would it then occupy?

4. 1 liter of oxygen measured under standard conditions weighs 1.429 g. What would 1 liter of the gas weigh when measured under each of the following conditions: (*a*) at 0° and a barometric reading of 740 mm? (*b*) at 50° and a barometric reading of 760 mm?

5. Suppose you have 1000 ml of oxygen under standard conditions. To what temperature should you have to cool it so that it would measure 500 ml, the pressure remaining constant?

6. To what temperature should you have to heat 1000 ml of air (measured under standard conditions) so that it would occupy 2000 ml at the same pressure?

CHAPTER V

Energy Changes, and Changes in Physical State

[Changes We Make Use of in Many Ways]

Further examples of transformation of energy. If we recall the differences between a gas, a liquid, and a solid, it will be clear that the change of a substance from one of these states into another must result in a change in its energy. For example, if we condense a gas to a liquid or a solid, the motion of its molecules is slowed down. What becomes of the energy of motion lost by the molecules? Or suppose we go in the opposite direction and change a solid into a liquid, and then into a gas. The molecules are now moving much faster, and their energy of motion has greatly increased. Where does this increased energy come from? We know that in neither case could it have been created or destroyed (p. 37).

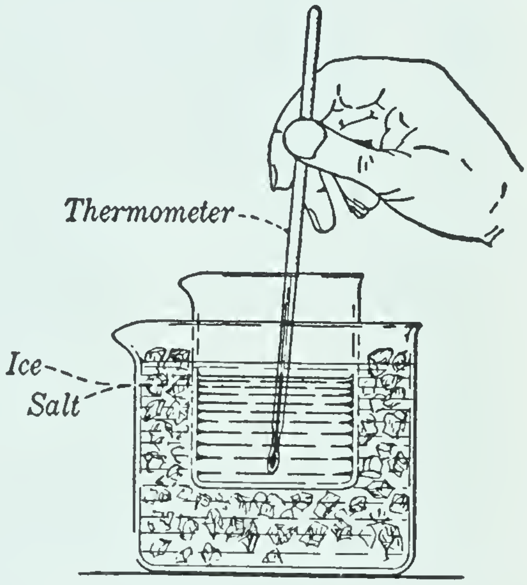


Fig. 33. Measuring the freezing point of water

The answers to these questions are of the greatest importance; for we shall find that these changes in energy affect our lives in many ways, and the operation of many important machines with which we are familiar depends upon them. To answer these questions we must have an understanding of a number of terms which the chemist uses, and which will be explained as we go along.

Freezing point and melting point. Suppose we put a beaker of pure water in a freezing mixture of salt and ice (Fig. 33). Let us keep stirring the water with a thermometer so that we can both watch the temperature and keep it the same in every part of the water. What will happen? Most of you know that the temperature will fall to zero, and the water will begin to freeze. *The temperature of the water will then remain exactly at 0° until all the water is frozen.* After that the temperature of the resulting ice will fall until it is the same as the temperature of the freezing mixture.

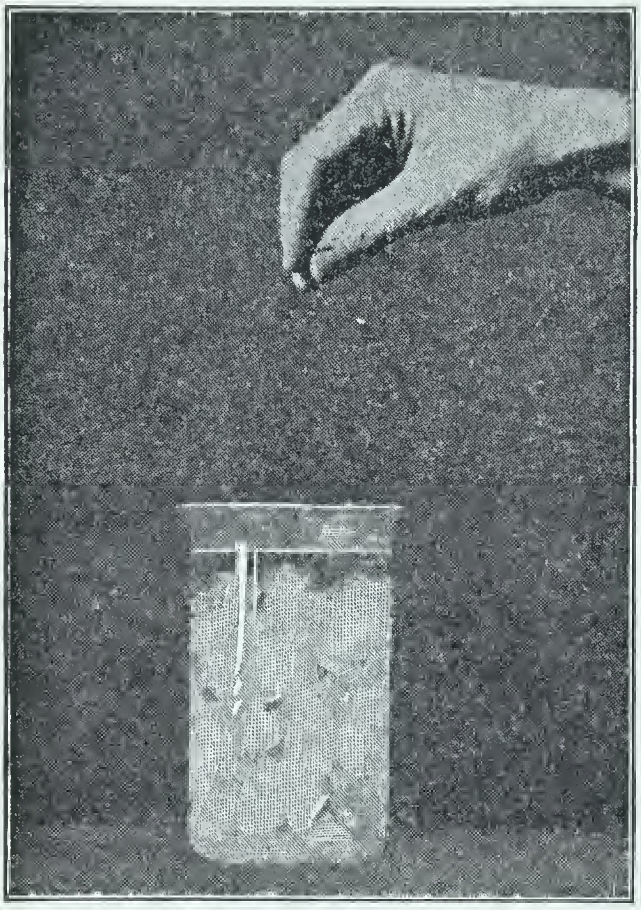


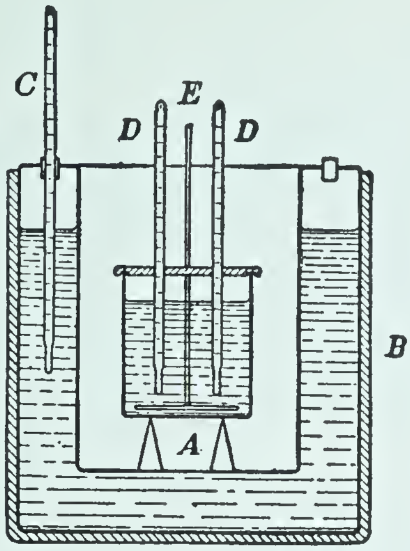
Fig. 34. An undercooled liquid quickly solidifies when a crystal of the solid is added

If we remove the beaker from the freezing mixture, reverse changes take place. The ice soon reaches the temperature of 0° and then commences to melt. *During the melting the temperature remains unchanged at 0°.* When all the ice is melted, the temperature slowly rises to that of the room. The unchanging temperature at which all the solid melts is called the *melting point* of the solid. Ice melts at 0°, lead melts at 327.5°, gold at 1063°. The melting point and the freezing point of a pure substance are always at the same temperature. We use the two terms instead of only one to show in which direction the change is taking place.

Summary: *The freezing point of a liquid is the constant temperature during the change of a liquid into a solid. The melting point of a solid is this same constant temperature during the change of the solid into a liquid.*

Undercooled liquids. Under unusual conditions a liquid may fail to begin forming crystals when its freezing point is reached and for some distance below that temperature. It is then said to be *undercooled.* When crystals finally do form, the temperature at once rises to the true freezing point. The formation of crystals in an undercooled liquid may be quickly started by dropping a fragment of the solid into the liquid (Fig. 34).

The melting of amorphous substances. Substances that have no crystal structure have no sharp melting point. When they are slowly heated, they usually become softer and gradu-



This figure shows the chief parts of a simple calorimeter. The vessel *A*, containing a definite weight of water, is placed within the double-walled vessel *B*, filled with water at room temperature. The substances are arranged so that the heat given off when they undergo change will be absorbed by the water in *A*. The thermometers *D*, *D* will measure the rise in temperature of the water in *A*, and the stirrer *E* will keep the temperature of the water uniform. Suppose the vessel *A* contains 1000 g of water, and the rise in temperature caused by the change is 2°; then the heat evolved is 1000 × 2, or 2000, cal

FIG. 35. A simple calorimeter

ally pass from the solid to the liquid state. If now the liquid is cooled, it slowly becomes thicker and more rigid until we usually call it a solid. Glass and sealing wax are such solids.

How do we measure heat? We have seen that heat is one of the forms of energy and that energy is the ability to do work. We easily see that the only way to measure energy of any kind is to measure the work it can do. We say that an engine has 60 horse power, by which we originally meant that it could do the work of 60 horses. The temperature of an object, as measured by a thermometer, gives us no idea of the heat it has in it — the work it can do. The tungsten wire in an electric lamp may be as hot as 2000°; but if we could suddenly dip this hot wire into a little water, we should not notice much change in the temperature of the water.

So we go about the measurement of a quantity of heat in a very practical way. Our *general plan* is to notice the effect a given source of heat can produce on some pure substance. We make this more definite by noting the extent to which the source of heat can raise the temperature of a specified weight of water. In this way we can soon agree on a *unit* for measuring heat, just as we agree on a yard or a meter stick for measuring distances. This unit is called a *calorie*, and its abbreviation is *cal*. The instrument used in measuring the heat given off or absorbed in any chemical change is called a *calorimeter* (Fig. 35).

The unit of heat energy (the calorie) is that quantity of heat that will raise the temperature of 1 gram of water through 1 degree of temperature.

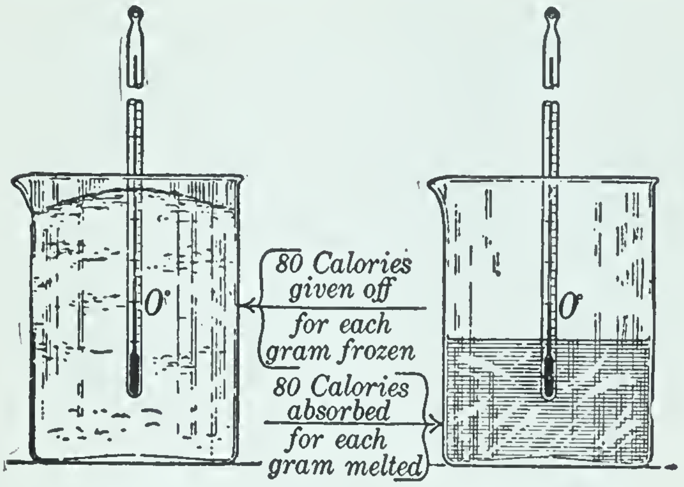

0°
80 Calories given off for each gram frozen
80 Calories absorbed for each gram melted
0°
Ice at 0°
Water at 0°

Fig. 36. The heat of solidification and the heat of fusion

Changes in heat energy during freezing and melting. The reason why the temperature of a liquid remains unchanged while the liquid freezes to a solid is that heat is given off in this process. It is only as this heat is conducted away that more of the liquid can freeze. The heat given off during the change of 1 g of a liquid at its freezing point into 1 g of solid at the same temperature is called the *heat of solidification* of that liquid. For water this is 80 cal. In other words, when 1 g of water at 0° changes into ice at 0°, 80 cal of heat is set free, or enough to raise the temperature of 1 g of water 80°. If we remember that in cold weather tons of ice form on the surface of a body of water, it is easy to understand why the accompanying heat changes should modify the climate.

When ice at 0° is melted, this heat change is in the other direction. It takes 80 cal of heat energy to melt 1 g of ice (Fig. 36). The heat used up in changing 1 g of a solid at its melting point into a liquid at that same temperature is called the *heat of fusion* of the solid. This heat energy is used up in the work of knocking apart the particles that compose the crystal. For the same substance the heat of solidification and that of fusion are the same in quantity.

Vapors: what they are. When exposed to the open air, a liquid, such as water, rapidly disappears at a rate that depends upon its surface and temperature. We say it *evaporates.* At its surface it is changing from the liquid state into a gas, which escapes into the air. If a substance is liquid or solid at ordinary temperatures, as is true of water or of ordinary moth balls, we call its gaseous state a *vapor.* So we speak of the vapor of water and not of the gas of water.

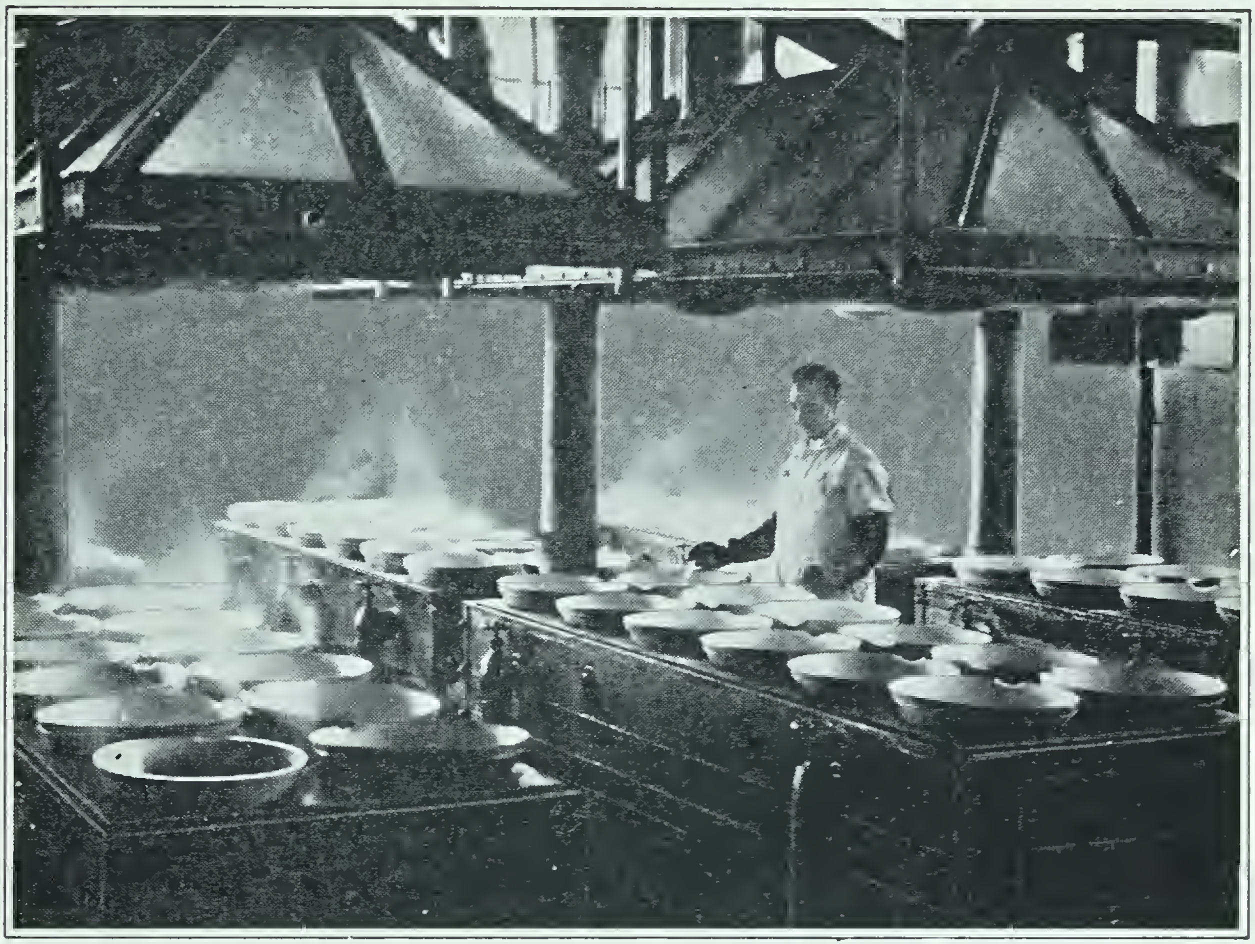


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FIG. 37. Evaporating liquids in the manufacture of chemicals. What is the advantage of having the vessels of the shape shown in the figure?

Vapors: how they are formed. The change of a liquid into a vapor is due to the violent motion of its molecules. Even though they have a great attraction for each other, some of them at the surface of the liquid are constantly breaking away and escaping into the air. This escape goes on at all temperatures, but *it is more rapid the higher the temperature.* This is because heat increases the average speed of the molecules, and more of them can break away (Fig. 37).

Even solids evaporate. The molecules of a solid, as we have seen, are also in constant motion, or vibration. However, their attraction for each other is so very strong that we might not expect them to escape into the air as do the molecules of a liquid. Yet we find that many solids do evaporate, although the rate of evaporation is so slow we do not notice it. Housekeepers know that when moth balls are exposed to the air they become smaller and smaller and finally disappear. The odor of many solids, such as camphor, is direct evidence that they evaporate.

When does a liquid boil? Suppose we heat a liquid in an open vessel; say, water in a beaker. The water evaporates, and the vapor so formed escapes into the air. But its escape is hindered by the air that presses upon the surface of the water. Each water molecule must fight its way through a throng of air molecules that oppose it. As the temperature is raised the rate of evaporation increases. The air molecules pressing upon the water are opposed by more and more water-vapor molecules until finally the vapor molecules are numerous enough to push back the whole opposing force of air molecules, just as one army becomes sufficiently strong to push back the opposing army. In scientific language we say that the pressure exerted by the vapor from the water finally exceeds the opposing pressure of the air.

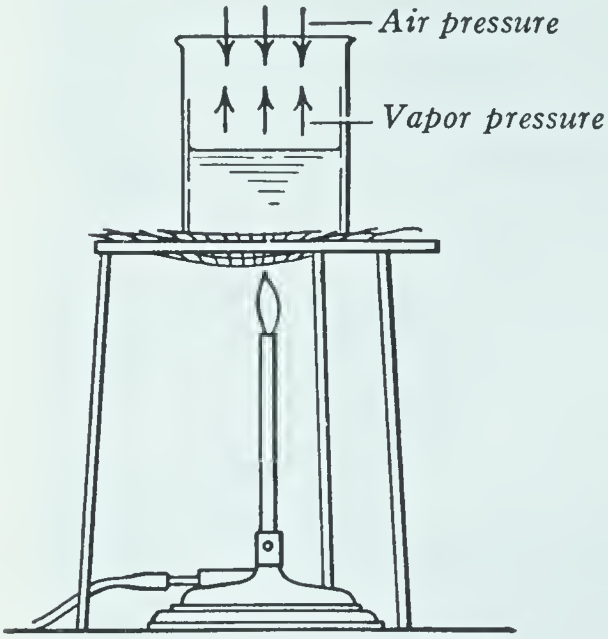


Fig. 38. Illustrating boiling point

The vapor pressure of the liquid in the beaker increases as the temperature of the liquid rises. The temperature at which the vapor pressure just exceeds the opposing air pressure is called the boiling point of the liquid

When this point is reached, there is nothing to prevent the vapor from escaping as fast as it forms, pushing the air before it. The heat now applied to the liquid water will no longer raise its temperature, but will merely hasten the rate of evaporation. The temperature at which this happens is the *boiling point* of the liquid (Fig. 38). With water the boiling point is 100°.

The boiling point of a liquid is the temperature at which its vapor pressure just exceeds the opposing air pressure.

Some questions. The thoughtful student will want to ask some questions. He knows that the pressure of the atmosphere is changeable. The barometer reads higher some days than others. Does the boiling point of a liquid also change with changes in atmospheric pressure? Yes, it does. At Mexico City (altitude, 7000 ft) water boils at 93°. On the top of Mt. Everest (altitude, 29,000 ft) it should boil at 72°, but no one has ever been there to prove this. When we say that water boils at 100°, we mean that this is its boiling point under standard pressure (p. 45).

Heat of vaporization. It takes heat energy to change a liquid into a vapor, just as it does to melt a solid. An equal amount of heat is given off when the vapor condenses to a liquid. The heat energy used to change 1 g of a liquid at its boiling point into vapor at the same temperature is called the *heat of vaporization* of this liquid. For water this is 537 cal. When the vapor so formed (1 g) is condensed to water again, 537 cal of heat are given off. This is called the *heat of condensation.*

How to change a gas into a liquid. In a given gas, as we have learned, the molecules are much farther apart than when in the liquid state, and have much greater kinetic energy. So to liquefy a gas, we push the molecules closer together by pressure and we diminish their energy by cooling the gas. Some gases are so easily liquefied that either pressure or cooling alone will liquefy them. Others, such as hydrogen and oxygen, are so difficult to liquefy that we must use the combined effect of both pressure and cooling.

Every known gas has now been liquefied. Helium, one of the gases used for inflating balloons, is the hardest of all to liquefy. Liquid helium boils at −268.9°. Liquid oxygen boils at −183°; liquid hydrogen, at −252.7°. Just as all gases have been liquefied, so all liquids have been solidified. Solid oxygen melts at − 218.4°, and solid hydrogen at − 259.1°. Solid helium melts at − 272.2°, a temperature very near absolute zero (p. 43).

Some practical applications. We have seen that heat is given off when a gas is compressed, as well as when a gas (or vapor) is liquefied; also that heat is absorbed when the reverse change takes place. The operation of many common machines, such as the steam engine, is made possible by taking advantage of these heat changes. One of these machines, the electric refrigerator, will now be described, and others will be described in appropriate places.

Electric refrigerators and how they work. These machines consist of two main parts separate from each other. In the one some suitable gas is liquefied by pressure, and the heat given off in the process is absorbed or conducted away. The resulting liquid is then run into the cooling compartment of the refrigerator, and the pressure lessened. The liquid then vaporizes rapidly, and the heat absorbed in this process lowers the temperature to the desired point. The resulting gas is conducted back to the condensing chamber, and the process is repeated (Fig. 39). A number of different gases are used in the refrigerators. The most common one has the formula CCl_2F_2, and the long name *dichlorodifluoromethane.* It is not poisonous and is rather easily liquefied by pressure alone (boiling point, −29.8°).

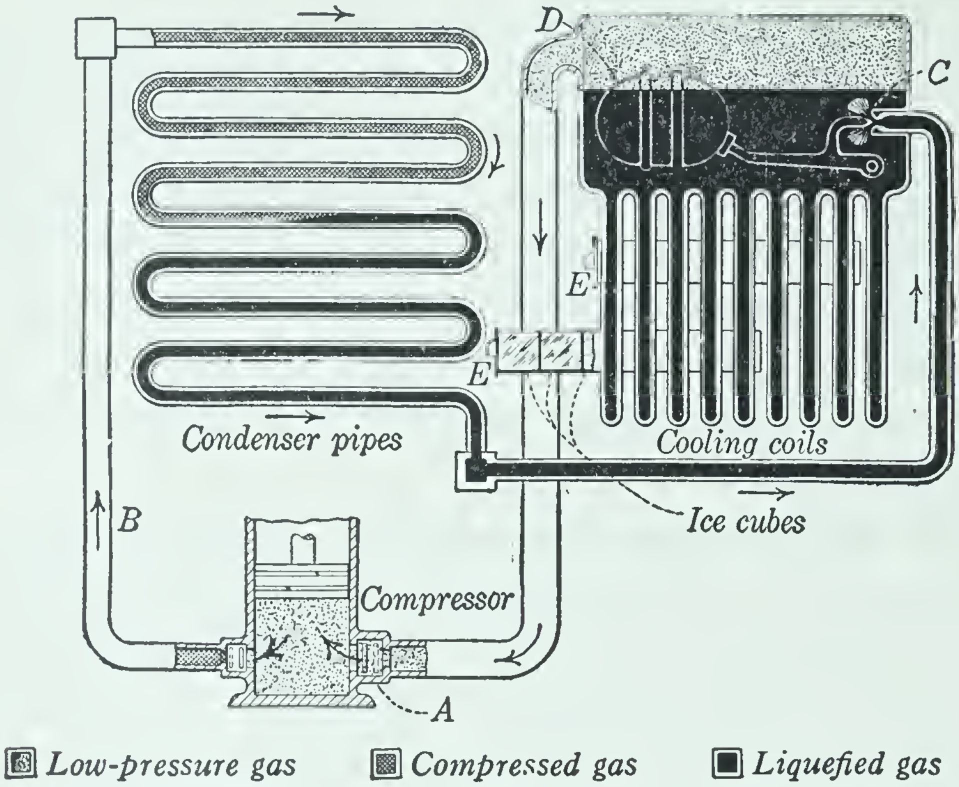


Fig. 39. Diagram to show how the electric household refrigerator operates

The gas enters the compressor at *A*. The compressed gas is forced upward through the pipe *B* and liquefies in the condenser pipes. The liquid then enters the icebox at *C*, where it evaporates, cooling the liquid in the coils. The evaporated gas returns to the compressor. The float-valve *D* regulates the circulation of the vaporized liquid. *E*, *E* represent the containers in which water is frozen to cubes of ice

CHAPTER SUMMARY IN QUESTION FORM

1. Show how changes in matter from one physical state to another are accompanied by changes in energy.

2. (*a*) What is meant by the *freezing point* of a liquid? (*b*) How is it found? (*c*) Illustrate in the case of water.

3. (*a*) What is meant by the *melting point* of a solid? (*b*) What kind of substances have a definite melting point?

4. How does the melting point of a substance compare with its freezing point?

5. (*a*) Do different substances have different melting points? (*b*) Does the same substance always have the same melting point?

6. (*a*) Give the name of the *unit of heat* and (*b*) define the unit.

7. (*a*) For what purpose is a calorimeter used? (*b*) Explain its construction and use.

8. What heat changes take place (*a*) when a liquid freezes? (*b*) when a solid melts?

9. Explain all the changes that take place (*a*) when water is cooled from 5° above zero until it is frozen; (*b*) when the resulting ice is warmed until it melts, and the water is heated to 5°.

10. Distinguish between vapors and gases.

11. (*a*) Give examples to illustrate the meaning of *evaporation.* (*b*) Name the conditions for rapid evaporation.

12. (*a*) Define the term *boiling point* and (*b*) illustrate it in the case of water.

13. What is understood when we say that water boils at 100°?

14. Define and give an example to illustrate each of the following terms: (*a*) heat of solidification; (*b*) heat of fusion; (*c*) heat of vaporization; (*d*) heat of condensation. Give the value of each of these for water.

15. State two ways by means of which the molecules of a gas can be crowded together to liquefy it.

16. Explain the working of a typical household electrical refrigerator.

THOUGHT QUESTIONS

1. (*a*) Is heat a form of matter or of energy? (*b*) When heat is applied to boiling water, the temperature is not raised; what becomes of the heat that is being applied?

2. Suggest a way (*a*) of raising the boiling point of water above 100°; (*b*) of lowering it below 100°.

3. Carbon dioxide is a gas rather easily liquefied. It is sold on the market compressed in strong iron cylinders. Do you think the carbon dioxide in such cylinders is in the form of a gas, a liquid, or some of both?

4. 1 liter of water at 10° was heated until it all boiled away. How many calories of heat were absorbed in the process?

5. What effect, if any, would a large body of water have on air temperature near it in (*a*) freezing weather? (*b*) during a thaw?

6. Some persons place tubs of water in their cellars on very cold nights, believing that this will keep the vegetables from freezing. Tell why you think this is wise or foolish.

7. 50 lb of ice (temperature, 0°) is placed in a refrigerator. How many calories of heat are absorbed in its melting? (See appendix for number of grams in 1 lb.)

8. Will water boil at the same temperature in New York as it does on Pikes Peak?

9. Will gold melt at the same temperature in New York as on Pikes Peak?

OPTIONAL EXERCISES

1. How should an air-hostess apply any of the facts stated in this chapter in cooking vegetables and boiling a "3-minute egg" while flying over high mountains?

2. 100 lb of ice (temperature, 0°) was placed in a refrigerator. It melted, and the resulting water flowing from the refrigerator had a temperature of 10°. How many calories of heat were absorbed from the interior of the refrigerator?

3. Do you think water really boils in the boiler of a steam engine?

4. Do you think it would be possible to cool a room by operating in it a household refrigerator, leaving the door of the refrigerator open?

5. What properties should a liquid have to make it suitable for use in a mechanical household refrigerator?

CHAPTER VI

Solutions

[Liquids We Are Using Every Day]

Some well-known liquids. Think over the liquids you know about: ordinary drinking water, sea water, milk, beverages of all kinds, vinegar, petroleum, various oils, sirups. Not one of them is a pure chemical compound; they are all solutions.

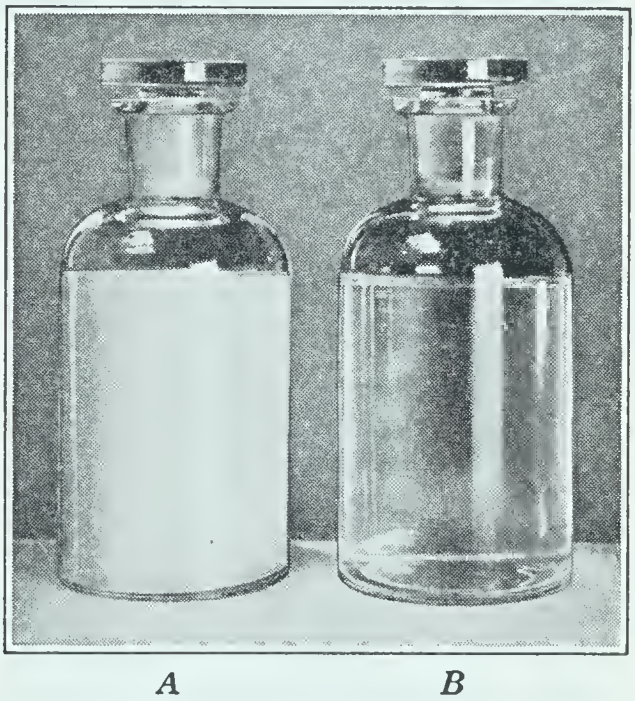


Fig. 40. A suspension and a solution

The bottle *A* is filled with a suspension of fine particles of clay. The bottle *B* contains a solution of salt

What is a solution? Everyone knows that when salt or sugar is stirred in water, the white solid disappears. The chemist says it *dissolves* in the water, and calls the resulting liquid a *solution.* He calls the dissolving liquid (water) the *solvent*, and the dissolved substance the *solute.* He says the salt and sugar are *soluble* in water. Most of the substances we shall meet in our study are soluble in water, at least to some extent. Even stones, glass, cements, and similar substances are slightly soluble; but so little dissolves that for practical purposes we call them *insoluble.*

All liquids are solvents. Every liquid is a solvent for something, although some of them may be very poor solvents. Alcohol and low-boiling gasoline are especially good solvents for fats and oils; so we often use gasoline for removing grease spots from our clothes. Water is by far the most general solvent for all classes of substances, and alcohol ranks high in the list.

All parts of a solution are the same. The most striking thing about a solution that has stood for some time, or has been well stirred (for stirring simply hastens the process of solution), is that any portion of it is just the same as any other portion. We dissolve sugar in our tea, and each drop of the tea has the same sweet taste. We can make this same fact evident to the eye by dissolving a minute crystal of a dye in water. The water becomes *uniformly* colored. That the solute must separate into very small particles is shown by the fact that a crystal of certain dyes no larger than a pinhead will distinctly color a liter or more of water. Indeed, we have good reasons for believing that the solute separates, as it dissolves, into its individual molecules, or, in the case of some solutes, into the atoms or groups of atoms composing it. These are much smaller even than the pores in a filter paper. So we cannot separate the solute from the solvent by filtration.

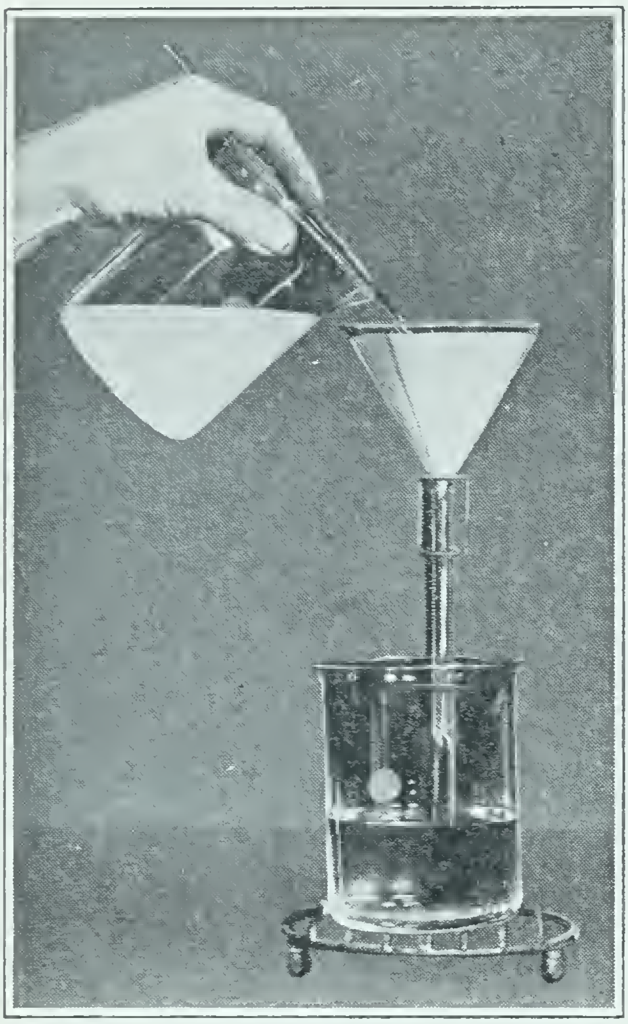


Fig. 41. Filtering a suspension. What do the results prove?

Suspensions. The ordinary mineral known as clay, and present in most soils, is insoluble in water. If we powder some clay very finely, and stir it in water, we get a milky or muddy-looking liquid. This is called a *suspension* (Fig. 40). The solid has not dissolved, and it slowly settles out from the water if we allow the mixture to stand quietly for a time. Any finely powdered solid, insoluble in a liquid, will form a suspension if stirred through the liquid. In all ordinary suspensions the solid can be removed by filtration (Fig. 41). In a true solution the solute will not settle on standing, neither can it be filtered out.

Chemical solutions. We sometimes say that zinc dissolves in sulfuric acid, just as we say that salt dissolves in water; for the zinc disappears in the liquid just as does the salt. But there is a real difference between the two cases. When we evaporate the solution of salt, we get back the salt with which we started. When we evaporate the zinc solution, we do not get any zinc, but a white solid, soluble in water, called zinc sulfate ($ZnSO_4$). Zinc itself is not soluble either in water or in sulfuric acid. When added to the acid, the zinc is changed into zinc sulfate, and it is this compound that remains in solution. That a real chemical action takes place is shown by the fact that we can see bubbles of gas escaping from the zinc as it dissolves, and we can prove that the gas is hydrogen. A solution that depends on a chemical action in this way is called a *chemical solution.*

Solutions differ from chemical compounds. Every portion of a chemical compound is exactly like every other portion in composition (p. 26). Every drop of a solution is exactly like every other drop in composition. What, then, is the difference between a chemical compound and a solution?

The difference is this. A compound — say, sugar — has one fixed composition, and we cannot change it in the least without destroying the compound. Solutions of the same substance, on the other hand, *may vary within wide limits in composition.* For example, we may add one lump of sugar to our cup of tea, or two or three lumps, although there is a limit to the amount of sugar that the tea will dissolve. If only a little solute is dissolved in a rather large volume of solvent, we call the solution a *dilute solution.* If the amount of solute is large in proportion to the solvent, we call it a *concentrated solution.* The sap of the maple tree is a dilute solution of sugar (and other substances); honey is a concentrated solution of several sugars.

A saturated solution. If we stir a little salt into a beaker half filled with water, it will quickly dissolve. If we add more salt, a little at a time, we shall presently find that no more salt will dissolve. We say the solution is *saturated.* As a matter of fact, we can prove by experiment that salt particles continue to dissolve, but at the same time other salt particles separate from the solution, forming crystals. At saturation the amount that dissolves exactly equals the amount that crystallizes out; so the concentration remains unchanged. The chemist expresses these facts by saying that a *balance*, or *equilibrium*, has been reached between the rate at which the solute dissolves and the rate at which it crystallizes out. We may give the following definition:

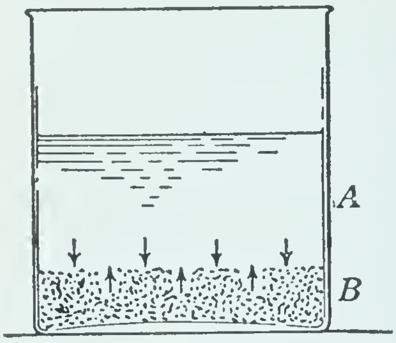


Fig. 42. A saturated solution

In a saturated solution *A* the amount of the solid *B* that dissolves is equal to the amount of the dissolved solid that separates

A saturated solution is one whose concentration remains unchanged while in contact with some of the undissolved solid (Fig. 42).

Illustration of saturation. The fact that saturation is an *equilibrium* of particles in motion, and not a condition of finished action, is illustrated by a familiar situation at a very popular continuous movie. The seating capacity at first rapidly fills up (the solid rapidly dissolves), then more slowly as seats become difficult to find, until at last all seats are occupied (saturation). A waiting crowd is left over (undissolved solid). Satisfied spectators keep leaving from time to time (crystallize out) and their places are promptly filled from the crowd (excess solid). This is now a state of equilibrium, and will continue as long as a waiting crowd (solid) is present, the seating capacity being always full but with changing individuals. We cannot be sure of complete saturation unless there is a waiting list. If it were possible to add a lot of chairs (corresponding to raising the temperature), there would be a new equilibrium with a larger audience (greater concentration).

The solubility of a substance. We often want to know how many grams of a substance it will take to make a saturated solution, or how many grams of it can be got by evaporating such a solution. This is called the *solubility* of the substance. To make an exact definition we must take into account both the solvent and the temperature. We can then say:

The solubility of a given solid at a given temperature is the weight in grams of the solid that will just saturate 100 g of the solvent.

A supersaturated solution. The solubility of most solids increases with the temperature. So a solvent, *saturated* at a

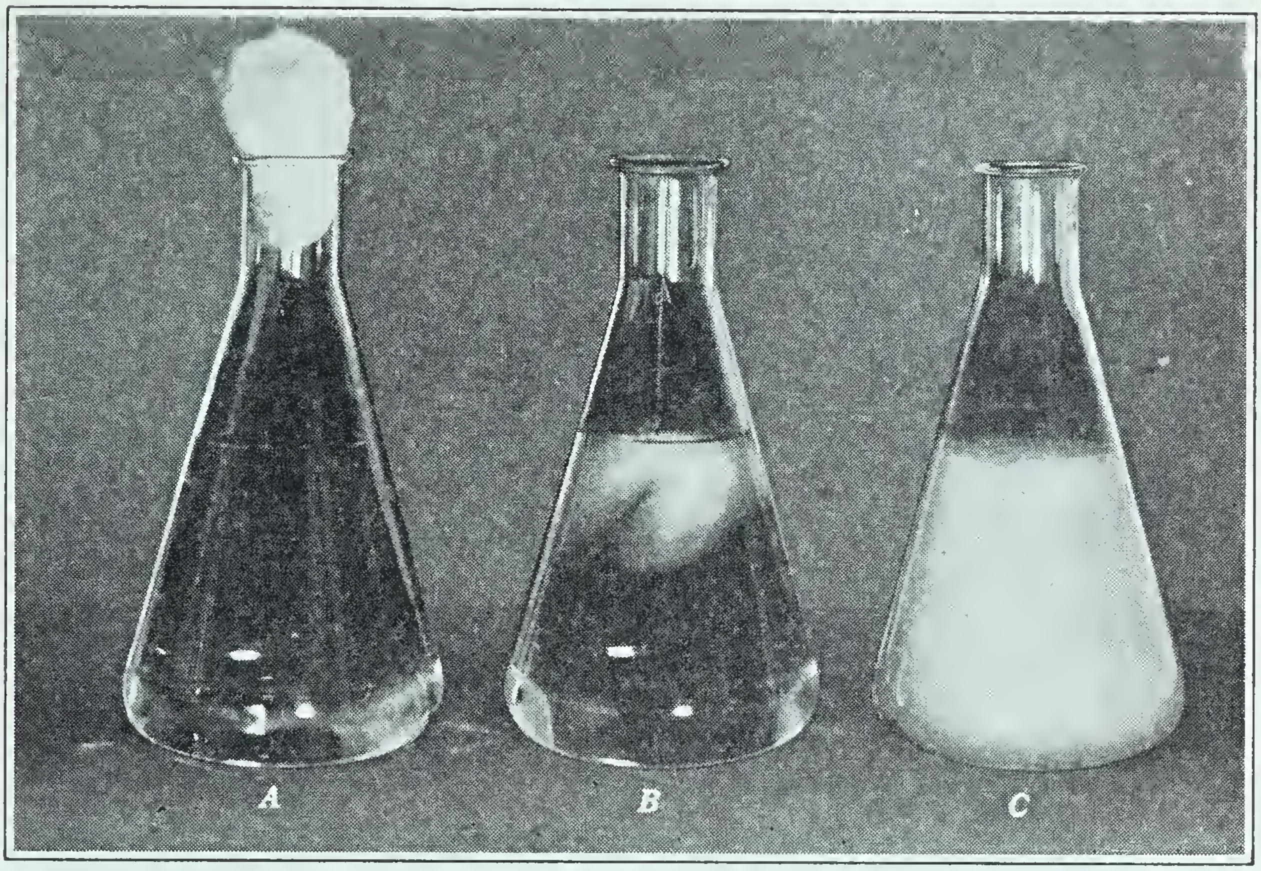


Fig. 43. An illustration of a supersaturated solution

Flask *A* contains a supersaturated solution of sodium acetate in water, prepared by saturating the water with the solid at a high temperature and then allowing it to cool. The cotton in the mouth of the flask is to prevent any solid particles from entering the solution while cooling. Flask *B* shows the solution a few seconds after dropping a minute crystal of sodium acetate into the solution. Flask *C* shows the solution about one minute after dropping in the crystal. The solid-looking mass is really a "mush" of fine crystals of sodium acetate

high temperature, steadily deposits crystals of the excess of the solute as the solution cools, while the solution remains saturated all the time.

If there are no crystals in the solution when it starts to cool, and it is not jarred or shaken in any way, it sometimes happens that no crystals form as the solution cools. The solution will then be holding more of the solute than is present at saturation. Such a solution is said to be *supersaturated.*

Supersaturation is an unbalanced condition. It is easy to show that supersaturation is an unbalanced condition. If even a very small crystal of the solute is dropped into a supersaturated solution, the excess of solute at once crystallizes out, leaving the solution saturated, as shown in Fig. 43.

Some jellies are supersaturated sugar solutions and on standing often deposit the excess of sugar crystals. Bees get a supersaturated solution (honey) in an interesting way. The solution they gather from flowers is rather dilute, and this

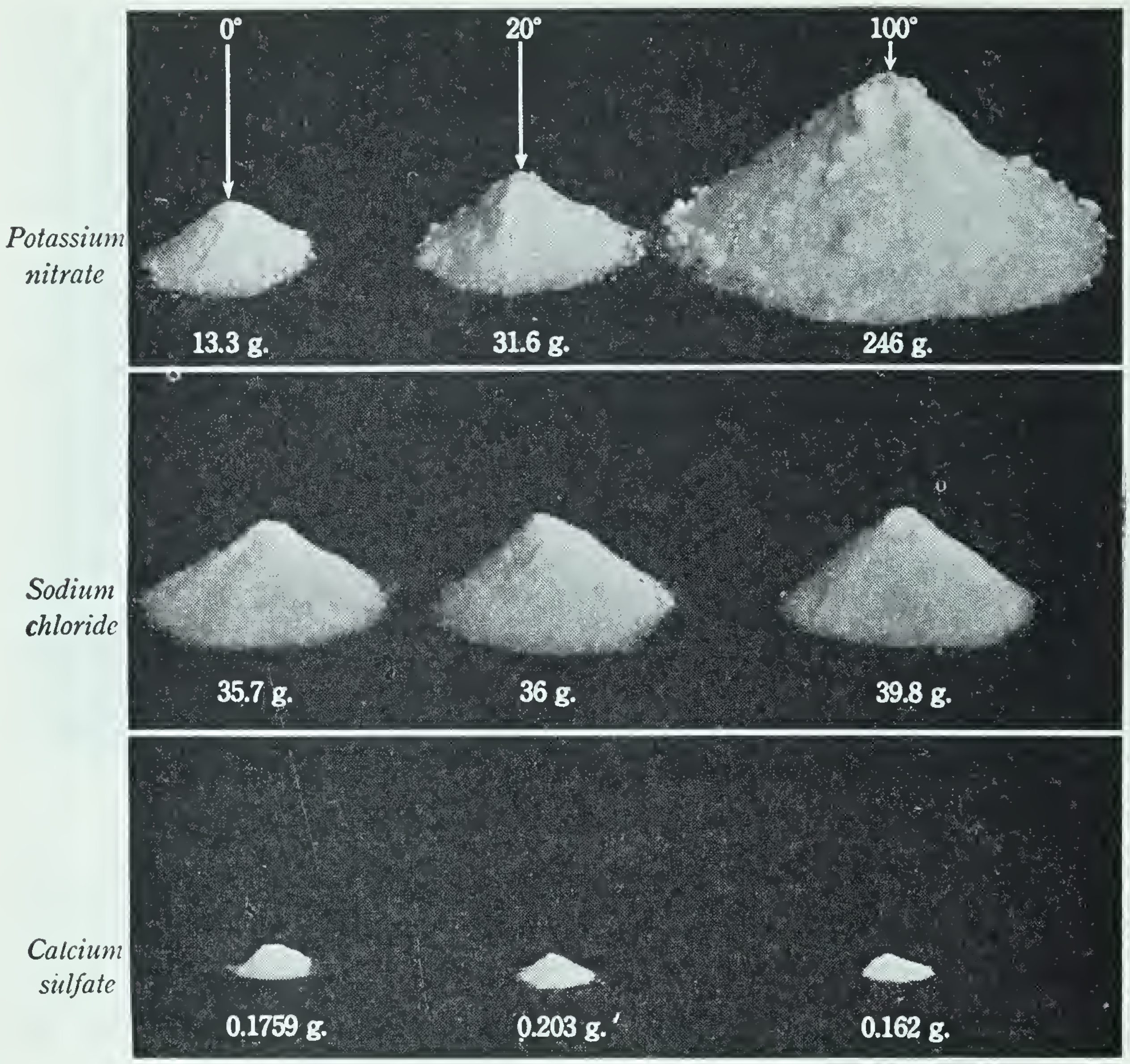


FIG. 44. The solubility of each of three compounds in 100 g of water at 0°, 20°, and 100°

What is the effect of increased temperature upon the solubility of each of the compounds?

they place in prepared cells of the honeycomb. A whole regiment of bees stay constantly in the hive, fanning this dilute solution with their wings to evaporate the water of the solution. Dilute solutions are added from time to time, and when the cells are closed the honey is much supersaturated. A factor which tends to preserve a state of supersaturation and thus helps the bees will be described later.

There are different kinds of solutions. There are a number of kinds of solutions other than the solution of a solid in a liquid. Every gas freely mixes with every other gas in all proportions, and such a mixture may be thought of as a solution of one gas in another. Gases and solids dissolve in liquids. One liquid often dissolves in another, or, in other words, the two liquids mix. (Such liquids are said to be *miscible.*) One solid sometimes dissolves in another. For example, if pieces of gold and lead are pressed tightly together, each metal very slowly dissolves into the other. The most familiar kind of solution is one in which a liquid is the solvent, and a gas, a second liquid, or a solid is the solute.

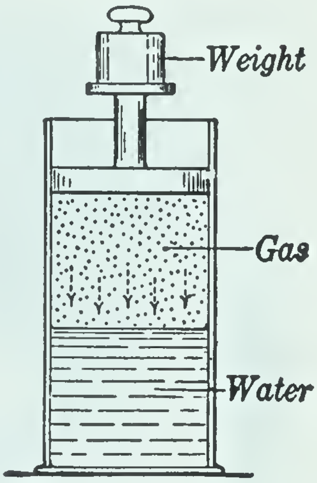


FIG. 45. Illustrating Henry's law

What effect would doubling the weight have upon the weight of gas going into solution?

Four things have an effect on solubility. Four things must be taken into account in stating solubility: the nature of the solute, the nature of the solvent, the temperature, and the pressure at which the solubility is measured.

1. ***The nature of the solute.*** Each substance has its own special solubility, just as it has its own color or taste or weight. All substances, whether solids, liquids, or gases, may be regarded as soluble *to some extent* in every liquid. But in many cases the solubility is too small to be measured. No one would think of copper as at all soluble in water, but it does have enough solubility to be poisonous to some low forms of life. Some solids dissolve in less than their own weight of water. Alcohol and water mix in all proportions. Ammonia gas dissolves to the extent of 1000 volumes in 1 volume of water.

2. ***The nature of the solvent.*** The nature of the solvent is just as special a matter as that of the solution. Water and alcohol have each their own solvent ability. Sugar is very soluble in water, but only slightly so in alcohol. Water is the most general solvent for all classes of compounds. Among the common solvents used in addition to water are alcohol, ether, carbon tetrachloride, and low-boiling gasoline, commonly called benzine.

3. ***The effect of temperature.*** The solubility of most solids *increases* with the temperature. At 100° water will dissolve nearly eight times as much potassium nitrate (common saltpeter) as the same weight of water at ordinary temperatures. With other solids, such as common salt, temperature has little effect. A very few solids are more soluble in

cold than in hot water. This fact is illustrated in Fig. 44, and is also shown in the table at the top of the next page.

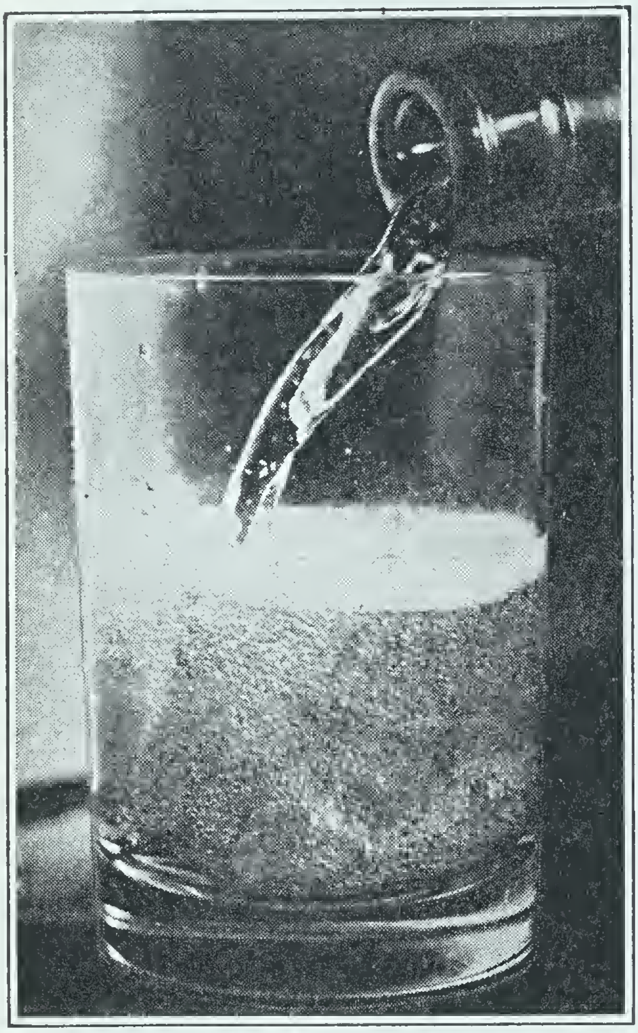


Fig. 46. The gas (carbon dioxide) escaping from ginger ale. Why does it escape?

This picture was taken with an exposure of $\frac{1}{100000}$ of a second. (Courtesy of *Technology Review*)

With gases the general effect is just the other way. *The lower the temperature of the solvent, the larger the volume of the gas it will dissolve.* By boiling a solution most gases can be completely driven out of the solvent.

4. ***The effect of pressure.*** Pressure has little effect upon the solubility of solids. But when we increase the pressure upon a gas standing over a liquid (Fig. 45), much more gas is forced into solution. With respect to any given solvent and gas we can make a general statement known as *Henry's law.*

HENRY'S *Law: Provided the temperature remains constant, the weight of a gas that dissolves in any given liquid is directly proportional to the pressure on the gas.*

If the pressure is doubled, the weight of the gas going into solution is also doubled. Under high pressure large quantities of many gases can be dissolved. When the pressure is removed, most of the gas escapes, causing the liquid to foam, or *effervesce.* Soda water is a familiar example of a liquid holding a gas (carbon dioxide) in solution under pressure, the usual pressure being about ten times that of the atmosphere. When the solution is withdrawn at the faucet, the pressure is reduced to a single atmosphere, and the additional gas escapes. All carbonated waters act in the same way (Fig. 46).

TABLE OF SOLUBILITY OF VARIOUS SOLIDS

SUBSTANCE	WEIGHT DISSOLVED BY 100 G OF WATER AT		
	0°	20°	100°
Calcium chloride	59.5 g	74.5 g	159.0 g
Sodium chloride	35.70 g	36.0 g	39.80 g
Potassium nitrate	13.30 g	31.6 g	246.0 g
Copper sulfate	14.30 g	20.7 g	75.4 g
Calcium sulfate	0.1759 g	0.203 g	0.162 g
Calcium hydroxide	0.185 g	0.165 g	0.077 g

Solubility tables and curves. It is important for chemists to keep in easily available form all the facts gathered by experiment about the solubilities of various substances. Many industrial processes depend for their success upon the solubilities of compounds formed. So solubilities are recorded in tables and by means of curves.

The table above gives the solubility of a number of solids at three temperatures. A study of this table will show how widely compounds differ in solubility. For example, at 0° potassium nitrate is only a little more than one third as soluble as sodium chloride, while at 100° it is more than six times as soluble. Calcium sulfate and calcium hydroxide are more soluble in water at 0° than at 100°.

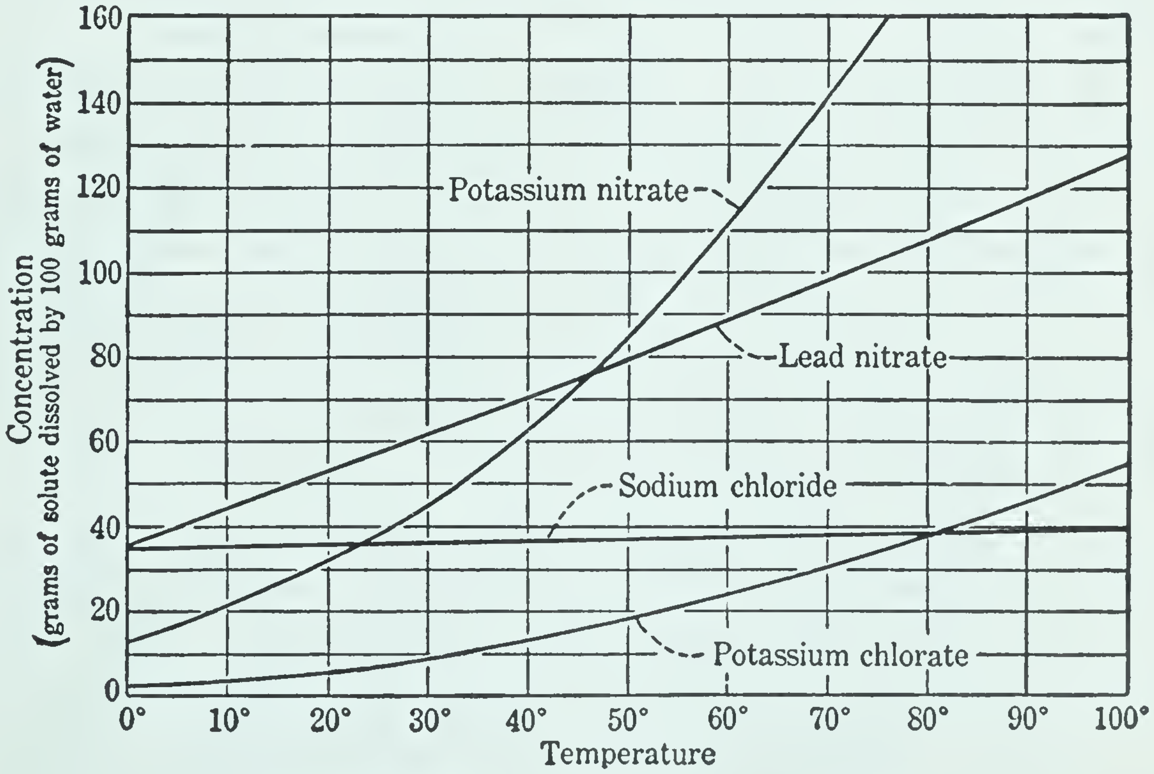


FIG. 47. Solubility represented by means of curves

Increase in temperature is represented in a horizontal direction, and increase in concentration in a vertical direction

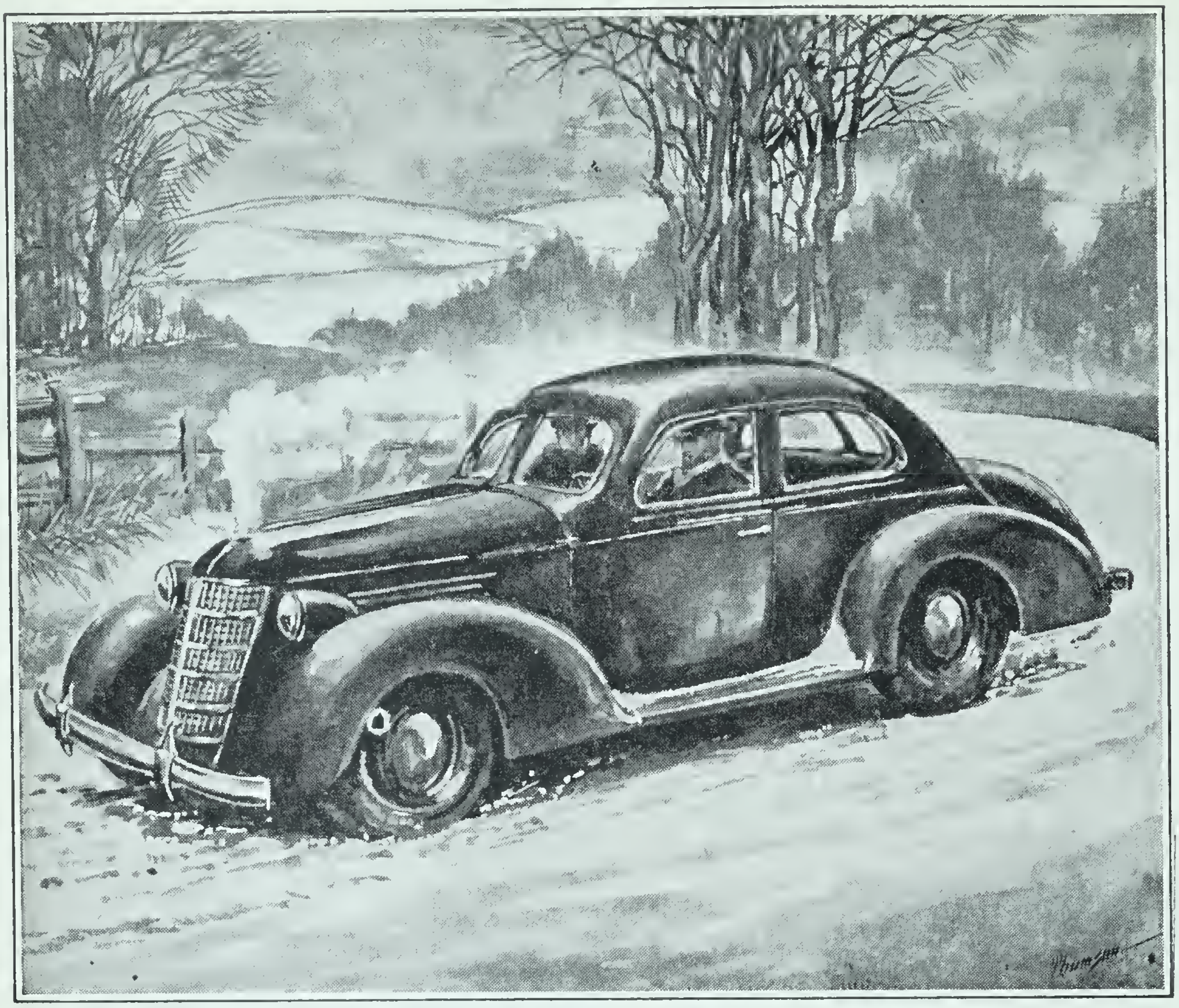


Fig. 48. What is the trouble here? How could it have been prevented?

Solubility curves (Fig. 47) are more convenient than tables and give more information. They give the solubility at *all* temperatures — not merely at a few stated points.

The boiling point of a solution. The boiling point of a solvent is *raised* by the presence of a dissolved solid. The more of a given solid dissolved in a definite weight of the solvent, the higher the boiling point of the solution. The boiling point of water saturated with a very soluble substance such as potassium nitrate may be as much as 15° or 20° above that of pure water (100°). So the boiling point of a solution varies with the concentration.

The freezing point of a solution. The freezing point of a solvent is *lowered* by a dissolved solute; and for a given solvent the more of the solute present the lower will be the freezing point of the solution. Ocean water will not form ice at 0°, and a saturated solution of a very soluble compound in water may not form ice until the temperature falls as low as −40° or −50°.

This explains why we put aqueous solutions of alcohol and of other compounds into the radiator of an automobile in winter (Fig. 48). Not only will the water not freeze so easily, but if the temperature should fall so low that it does freeze, it forms only a mush of small ice crystals, and not a solid cake that can burst a metal tube. If we use denatured alcohol (about 90 per cent alcohol), the temperatures at which ice crystals form are as follows:

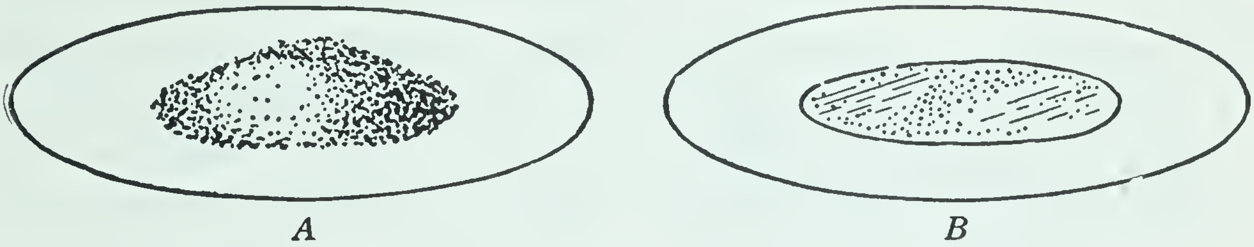


FIG. 49. Illustrating deliquescence. The deliquescent compound *A*, on exposure to air, absorbs moisture and forms the solution *B*

Percentage by volume of alcohol in water	10	20	30	40	50
Freezing point, centigrade	− 3°	− 7°	− 12°	− 19°	− 28°
Freezing point, Fahrenheit	+ 27°	+ 19°	+ 10°	− 2°	− 18°

Many cheap soluble salts, such as calcium chloride, would prevent freezing just as well as alcohol; but they all tend to damage the metal tubes of the radiator, especially where these are soldered together.

Deliquescent compounds. This means "liquid-forming" compounds. Although we may not realize it, it is a fact that all the solid objects about us — the furniture of the house, the dishes, the windows, the walls — tend to gather (or *adsorb*) a film of moisture on their surfaces. In the large words of science, they are said to be somewhat *hygroscopic*.

Some very soluble compounds adsorb so much moisture that they are damp to the touch, as is true of impure salt. In more extreme cases the compound may gather so much water from the air that it gradually passes into solution. Such a compound is said to be *deliquescent* (Fig. 49). Calcium chloride, used to dry hydrogen and sometimes to lay the dust on tennis courts and roads, is a deliquescent compound.

Electrolysis of solutions. One of the most interesting properties of a solution is the way it acts toward an electric current. Pure water conducts the current hardly at all; the same is true of water in which certain compounds have been dissolved, such as sugar or alcohol. Water, sugar, alcohol, and all other compounds whose solutions do not conduct the electric current are called *nonelectrolytes.*

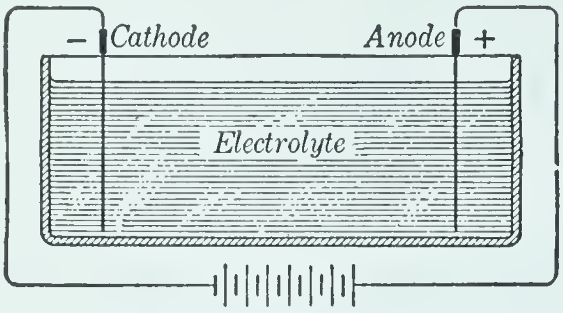


FIG. 50. The electrolysis of a solution of an electrolyte

But if certain other compounds, such as common salt or sulfuric acid, are dissolved in water, the resulting solutions are good conductors. Compounds whose solutions are conductors are called *electrolytes.* When an electric current passes through a solution of an electrolyte, a chemical change always takes place in the solution. This is called *electrolysis.*

Electrolysis is the chemical change that takes place when an electric current passes through a solution of an electrolyte.

An electrolytic cell. The general plan used in the electrolysis of a solution is illustrated in Fig. 50. Two plates or rods made of suitable material, such as carbon or some metal, are connected with the wires from a battery or dynamo, and dipped into the solution as shown in the figure. These plates or rods are called *electrodes.* The electrode connected with the positive pole of the battery is the positive electrode, or *anode*; that connected with the negative pole is the negative electrode, or *cathode.* An arrangement of this kind is called an *electrolytic cell.* The particular form of apparatus used varies in individual cases. In the electrolysis of water (Fig. 19) the electrodes are so arranged that the oxygen and hydrogen produced may be collected separately.

Where does electrolysis take place? Since it is clear that *in some way* the electric current passes through the conducting solution from one electrode to the other, it might be expected that chemical action (electrolysis) would be noticed all through the solution. This is not the case. The only visible effect of the current is at the surfaces of the electrodes. The explanation of this singular fact will be found in a later chapter.

Industrial importance of electrolysis. Many of the chemical changes produced by electrolysis are of the greatest importance in the industries. For example, the metal aluminum, so largely used in making automobiles, airships, and cooking vessels, is obtained entirely by electrolysis. By this means also copper and other metals are purified, and various objects are plated with gold, silver, nickel, and chromium (electroplating).

CHAPTER SUMMARY IN QUESTION FORM

1. Suppose you stir some salt in water until the salt disappears. What name is given (*a*) to the resulting liquid? (*b*) to the salt? (*c*) to the water?

2. Name some good solvents, and some substances that will dissolve in each.

3. (*a*) Name an important characteristic of a solution. (*b*) What is the distinction between a solution and a suspension?

4. (*a*) What is a chemical solution? (*b*) Give an example.

5. Explain what is meant by each of the following terms, and illustrate each by an example: (*a*) dilute solution; (*b*) concentrated solution; (*c*) saturated solution; (*d*) supersaturated solution.

6. What do we mean by the phrase "solubility of a solid in a liquid"?

7. Name the different classes of solutions.

8. Name the different factors that affect the solubility (*a*) of a solid in a liquid; (*b*) of a gas in a liquid.

9. Name (*a*) a compound that is only slightly soluble in water at any temperature; (*b*) one that is much more soluble in hot water than in cold; (*c*) one that is about equally soluble in hot water and in cold; (*d*) one that is more soluble in cold water than in hot (see table, p. 71).

10. (*a*) Explain why soda water effervesces. (*b*) What law does this illustrate?

11. What effect has a dissolved solid on (*a*) the boiling point of a liquid? (*b*) the freezing point of a liquid? (*c*) Give a practical application of each of these effects.

12. Give the words that we apply to each of the following compounds: (*a*) one that becomes moist on exposure to air; (*b*) one that attracts so much moisture from the air that it passes into solution.

13. (*a*) Distinguish between electrolytes and nonelectrolytes. (*b*) Give examples of each.

14. Draw a diagram and illustrate by it the meaning of each of the following words: (*a*) electrolyte; (*b*) electrode; (*c*) cathode; (*d*) anode; (*e*) electrolysis.

THOUGHT QUESTIONS

1. How can you tell whether a given solution is (*a*) unsaturated, (*b*) saturated, or (*c*) supersaturated?

2. Any two samples of a compound have the same composition; any two drops of a given solution have the same composition. What is the difference between a compound and a solution?

3. Explain the meaning of the statement "The solubility of sodium chloride at 20° is 36 g."

4. Calcium chloride is used to lay the dust on roads. What property does it have that makes it useful for this purpose?

5. Does soda water effervesce when inside the fountain or only when withdrawn?

6. When salt is dissolved in water and the water is evaporated, the salt is again obtained in the solid state. If zinc is dissolved in sulfuric acid and the liquid is evaporated, not zinc but a white solid is obtained. Explain.

7. By reference to the solubility curves, Fig. 47, find the solubilities of the following compounds at the temperatures indicated: (*a*) potassium chlorate at 10°, at 50°, at 100°; (*b*) lead nitrate at 30°, at 90°; (*c*) sodium chloride at 10°, at 50°, at 100°.

8. At what temperature is the solubility of potassium nitrate the same as (*a*) that of sodium chloride? (*b*) that of lead nitrate?

9. 100 g of water at 100° is saturated with potassium chlorate. The resulting solution is reduced to room temperature (20°). What weight of potassium chlorate will be deposited?

10. How could you measure the solubility of a compound?

11. Give an example of a chemical change caused (*a*) by heat; (*b*) by light; (*c*) by electricity.

OPTIONAL EXERCISES

1. Ordinary household camphor (tincture of camphor) is a solution of the white solid known as "camphor gum" in alcohol. This gum is insoluble in water. Predict what will happen if water is added to the tincture of camphor. If possible, test your prediction by experiment.

2. Prepare a paper giving the names and statements of all the laws so far studied.

3. Which of the following statements are true and which false?

(*a*) Sodium chloride (common salt) is more soluble in hot water than in cold.

(*b*) Calcium hydroxide (hydrated lime) is more soluble in hot water than in cold.

(*c*) 25 g of sodium chloride will dissolve in 100 g of boiling water.

(*d*) 50 g of calcium chloride will dissolve in 100 g of water at room temperature.

(*e*) At 50° 100 g of water will dissolve more potassium chlorate than sodium chloride.

UNIT READINGS

CLARKE. *Marvels of Modern Chemistry.* [Read pages 76–81, "The Language of Chemistry."]

FOSTER. *The Romance of Chemistry.* [Read Chapter II, "Things Seen and Unseen"; this deals with matter and energy. Read also Chapter IV, "Chemical Elements and Compounds."]

HAYES. *What Makes Up the World.* [Read Chapter V, "Earth"; also Chapter VI, "Changes." Very elementary but interesting.]

HOLMYARD. *Chemistry for Beginners.* [Read pages 97–113, a popular and fascinating discussion of atoms, molecules, formulas, and equations.]

JAFFE. *Crucibles.* [Chapter VII gives an interesting account of Dalton and his ideas of atoms.]

MOORE. *History of Chemistry.* [Read Chapter IV, "Boyle and His Contemporaries."]

ROSE. *Journal of Chemical Education,* Vol. 6, p. 1797, "How Small is a Molecule?"

STEVENS. *The National Geographic Magazine,* Vol. LXIX, p. 59, "Man's Farthest Aloft." [Read the article and point out any applications of Boyle's law and Charles's law.]

WEEKS. *The Discovery of Elements.* [Find in the index the names of the elements with which you are familiar; then read of their discovery.]

The Science Leaflet. [Read pages 142–148 of Volume X, on "Energy"; also pages 457–461 of Volume XI, on "The Kinetic Theory of Gases."]

Unit Three. The Chemistry of Three Common Elements

WE ARE apt to think very little concerning the common things about us and to be much carried away by some rare thing. We wonder at the glowing color and sparkle of a ruby, but pay little attention to a glass of water or a lump of coal.

Now these common things that we need every day and that we use for many purposes are really the most wonderful of all. A ruby is remarkable for but a few qualities: its color, its sparkle, its hardness, and its cost. It is important in one way only — as a jewel. While it may interest us, we could get along just as well without it. The substances that are really necessary for our lives as well as for our comfort are, as a rule, abundant and low in cost. Among all these, water would probably be considered as the most important.

In this unit we shall study the composition and properties of water. Since it is composed of oxygen and hydrogen, we shall begin our study with these two elements, and see how they combine in one proportion to form water and in another to form an entirely different compound, hydrogen peroxide. We shall see how the chemist found out the exact composition of water, and how he determines the composition of any pure compound. We shall also study the element carbon, since it is present in such common substances as coal and most of our foods; also the two oxides of carbon — gases that we meet in our everyday life.

The information gained in our study of these various substances will let us see how a number of very striking laws of chemistry have been found that state the way in which substances act upon each other.

CHAPTER VII

Oxygen

[The Most Abundant of All the Elements]

Joseph Priestley and his great discovery. About two hundred years ago there was born in England a boy whose name, Joseph Priestley, has since become familiar to every chemist. Young Priestley studied for the ministry, and at the age of twenty-two began to preach. Some of the people were not pleased with his religious and political views, and finally they showed their displeasure by burning his church and mobbing his house. As a result of such treatment Priestley came to America (1794) and settled in Northumberland, a little town in the mountains of Pennsylvania, where he spent the rest of his life (Fig. 53).

But Priestley was not only a minister; he was by nature a true scientist. He had an eager mind, keen powers of observation, and a great desire to know the truth about all things. Most of all, he liked to experiment with gases, or "airs" as he called them (Fig. 52); and it is chiefly by his discovery of six or eight important gases and his study of their properties that we remember him. He often heated substances to see if he could get a gas out of them.

One day (August 1, 1774) he put a small amount of mercuric oxide (HgO) into a tube, filled it with mercury, and then turned it upside down in a vessel of mercury, as shown in Fig. 51. The oxide, being lighter than liquid mercury, rose to the top of the tube. Priestley then heated the solid oxide by focusing the sun's rays upon it with a large glass lens. He soon found that a gas was given off which collected in the top of the tube. Describing this result he afterward wrote, "What surprised me more than I can well express was that a candle burned in this air with a remarkably brilliant flame." This "air" was none other than the gas we now call *oxygen*, and we think of Priestley's discovery of it as one of the great turning points in the history of chemistry. It led the great French chemist Lavoisier (Fig. 58) to find out just what takes place when a substance burns. It seems certain that other chemical workers, notably the Swedish chemist Scheele (Fig. 147), had prepared oxygen before Priestley. But the credit for the discovery of an element goes to the one who first publishes his results and tells all about them, and Priestley was the first to do this for oxygen.

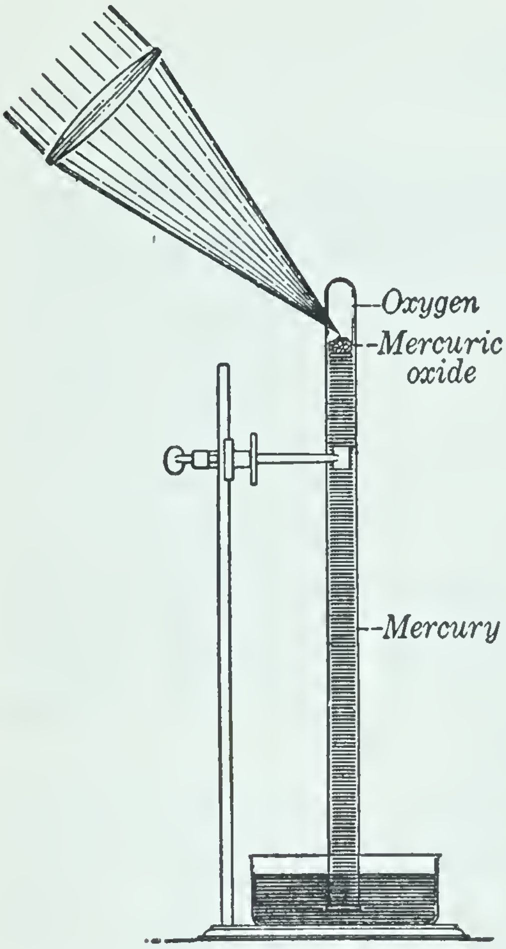


Fig. 51. Priestley's way of getting oxygen by heating mercuric oxide

What keeps the mercury up in the tube?

Where is oxygen found? Oxygen is in us and all about us. The atmosphere is the great storehouse of free oxygen. If we were to separate 100 liters of dry air into the gases that compose it, we should have about 21 liters of oxygen, 78 liters of nitrogen, and 1 liter of other gases. There are millions of tons of free oxygen in the earth's atmosphere. Combined with other elements, oxygen forms eight ninths, by weight, of water; nearly one half of the rocks that form the earth's crust; and over half of all the plants and animals, our own bodies included (see page 30).

To get pure oxygen is a problem. While oxygen is so abundant in nature, it is always either mixed with other gases, as in the air, or combined with other elements in compounds, such as water. Just how to obtain it free from all other substances is therefore an important problem. Since air costs nothing, we should naturally try to obtain it from this source. But the separation of oxygen from the other gases with which it is mixed in the air is a difficult matter, requiring expensive machinery. So this method is used only when large quantities of oxygen are wanted for commercial purposes (Fig. 54). In the laboratory, where only small quantities are needed for a study of the properties of the element, oxygen is prepared by decomposing certain of its compounds. The ones best suited to this purpose are (1) mercuric oxide, (2) water, and (3) potassium chlorate.

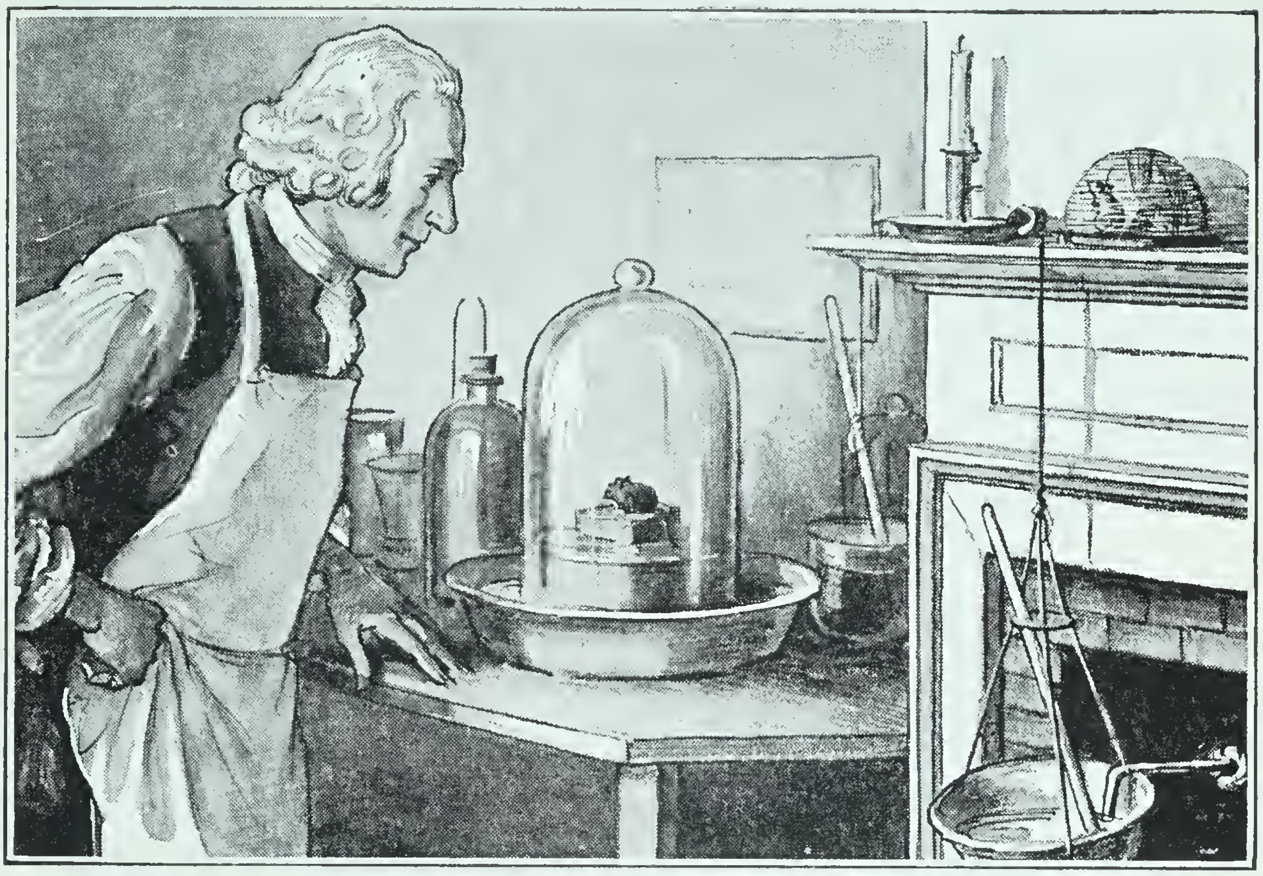


Fig. 52. Joseph Priestley (1733–1804) in his laboratory, carrying on experiments to find out if mice could live in his newly discovered gas (oxygen)

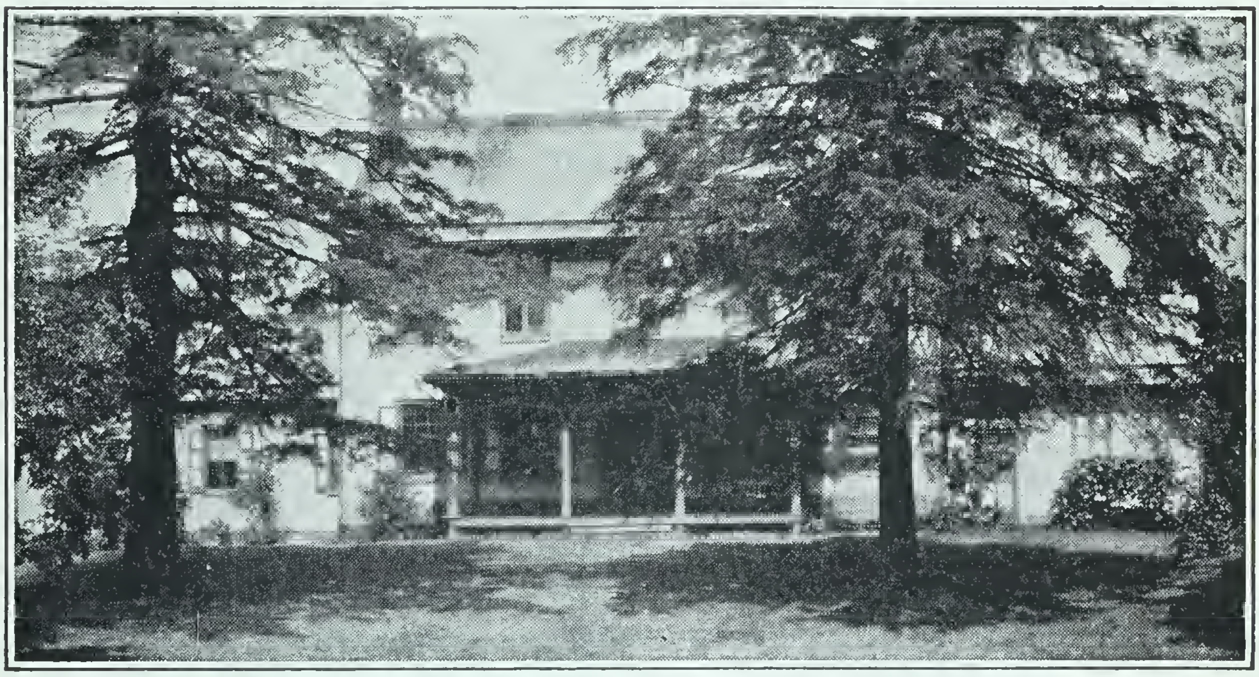


Fig. 53. Priestley's home at Northumberland, Pennsylvania

It has been repaired and is kept open to visitors as a memorial to him. A small laboratory, near by, contains his scientific apparatus

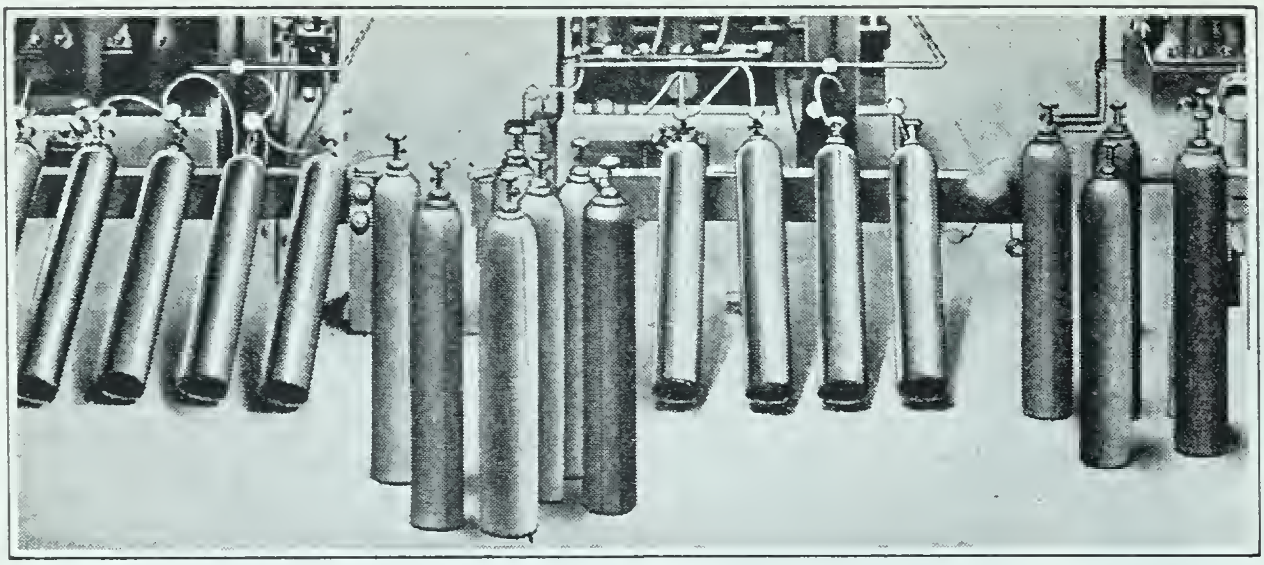


FIG. 54. Oxygen stored in strong steel cylinders for sale on the market. Why must the cylinders be strong?

1. ***Oxygen from mercuric oxide.*** This method is too expensive for ordinary use, but it is of interest because it is the one that led Priestley to discover oxygen. Mercuric oxide is a compound consisting of 7.4 per cent of oxygen and 92.6 per cent of mercury. When this compound is heated, it decomposes into mercury and oxygen (p. 33); and we have learned to represent this change as follows:

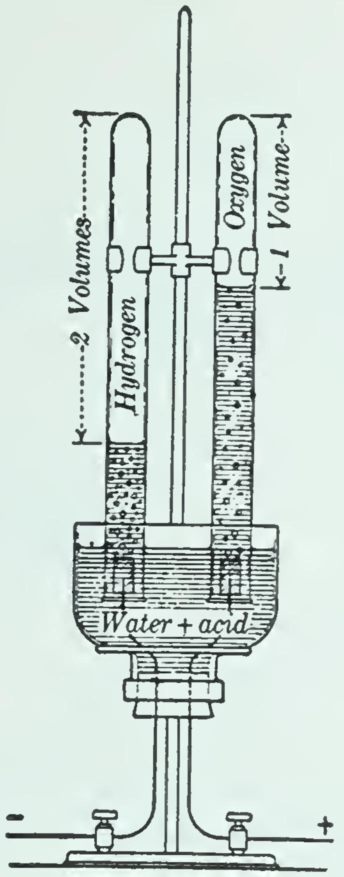
$$2\ HgO \longrightarrow 2\ Hg + O_2$$

2. ***Oxygen from water.*** We have learned (p. 26) that water is a compound containing 88.81 per cent oxygen and 11.19 per cent hydrogen by weight. Though it is very difficult to separate it into its elements by heat, it can be decomposed easily by the use of electrical energy, as shown in Fig. 55.

Since the formula of water is H_2O (p. 34), the reaction that takes place when water is decomposed may be represented in the following shorthand way:

$$2\ H_2O \longrightarrow 2\ H_2 + O_2$$

This equation tells us not only that water decomposes into hydrogen and oxygen, but also that the atoms of both of these gases, as fast as liberated, combine to form molecules, each made up of two atoms (p. 34). The exact translation of this equation would read as follows: Two molecules of water decompose into two *molecules* of hydrogen and one *molecule* of oxygen. Of course, the method just described



Two tubes entirely filled with water containing a few drops of sulfuric acid are inverted in a vessel of the same liquid, as shown in the figure. Into the mouth of each tube extends a piece of platinum foil attached to a wire. These wires are connected with a battery supplying from 6 to 10 volts. The electric current flows from one wire to the other through the water. The water is decomposed by the current into oxygen, which escapes from one of the pieces of platinum (the anode), and hydrogen, which escapes from the other (the cathode). The gases, being much lighter than water, rise in the tubes and are collected as shown in the figure

FIG. 55. Apparatus for preparing oxygen (and hydrogen) by decomposing water by the electric current

can be used equally well for the preparation of hydrogen, which we shall study in the next chapter. It is very striking that *the volume of the hydrogen liberated is just twice that of the oxygen.* The importance of this fact will be referred to many times in later chapters.

3. ***Oxygen from potassium chlorate.*** This is the method we nearly always use in the laboratory. Potassium chlorate is a white solid composed of the three elements potassium, chlorine, and oxygen. Its formula has been found to be $KClO_3$, and it contains 39.2 per cent oxygen. When it is heated above its melting point, the oxygen is set free as a gas, and a white solid is left. This solid is composed of potassium and chlorine, its formula is KCl, and it is called potassium chloride. The equation

$$KClO_3 \longrightarrow KCl + 3\ O$$

expresses the facts we have just stated. But we have seen (p. 33) that oxygen *atoms* immediately unite *in pairs* to form oxygen *molecules*, O_2. To represent this additional fact we must double this equation so as to get an *even number* of oxygen atoms. We then have:

$$2\ KClO_3 \longrightarrow 2\ KCl + 3\ O_2$$

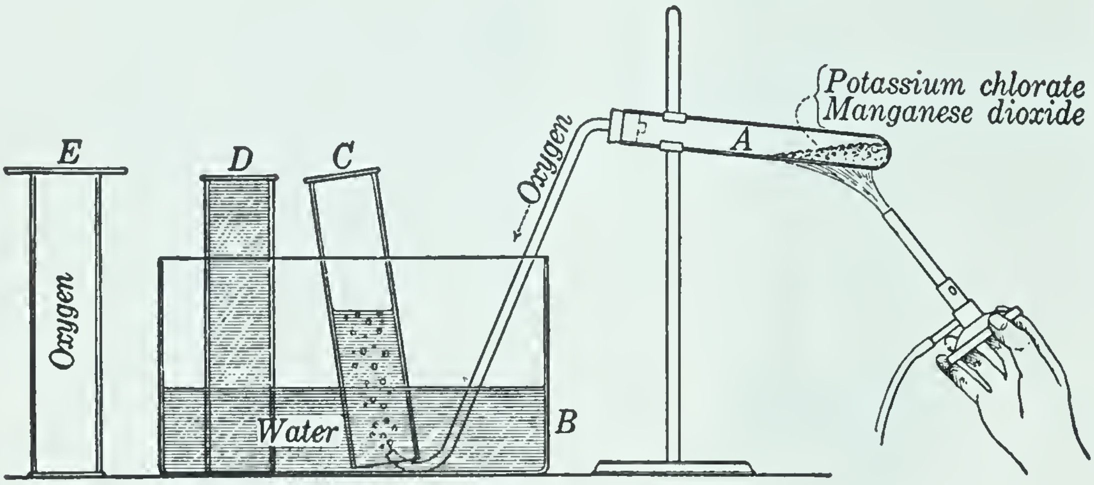


Fig. 56. The preparation of oxygen from potassium chlorate

The chlorate is first mixed with a little manganese dioxide, and the mixture transferred to the tube *A* and gently heated. The oxygen in the potassium chlorate is given off and escapes through the exit tube. It is collected by bringing over the end of the tube a cylinder *C* completely filled with water. The gas rises in the cylinder and displaces the water

We read this equation as follows: Two molecules of potassium chlorate decompose into two molecules of potassium chloride and three molecules of oxygen.

A catalytic agent the "oil can" of chemical action. Every one knows that when the lawn-mower or the carpet-sweeper or the bicycle begins to run hard, it is time to get the oil can and put a few drops of oil in the right places. Strangely enough, many chemical actions "run hard," especially at the start. And more surprising still is the fact that we can often speed up the reaction by adding some other substance to the reacting mixture, just as we add oil to machinery. These added things merely make the reaction go faster, more smoothly, and at a lower temperature. They are called *catalytic agents* or simply *catalysts*.

In the preparation of oxygen from potassium chlorate it has been found that a small quantity of the black mineral called manganese dioxide is a good catalyst. So we always add it to the chlorate before we heat it (Fig. 56). It does not enable us to get *more* oxygen, but it does help us to get it more steadily and with less heating. We shall see that many industrial processes depend on suitable catalysts for their success.

Physical properties of oxygen. In preparing oxygen about all we can notice of its properties is that it is a gas and that it has no odor, taste, or color. Since we collect it over water, we may guess that not much of it dissolves in the water. More exact *measurements* show that about 4 volumes of the gas dissolve in 100 volumes of water (under the conditions of temperature and atmospheric pressure that are usual in the laboratory). It is slightly heavier than air.

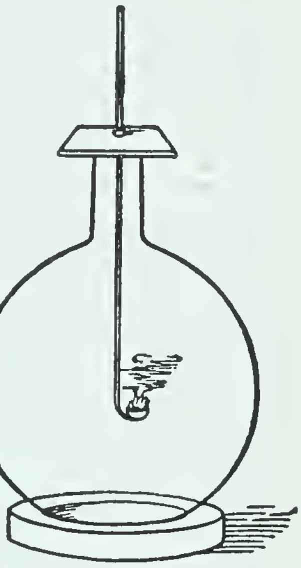


Fig. 57. Burning sulfur in oxygen

Chemical conduct of oxygen. Since there is so much oxygen in the air, it is clear that at ordinary temperatures it cannot be very active chemically. Yet it does act *very slowly* on many things. During weeks and months of exposure to air, iron rusts, copper tarnishes, paints fade, wood rots, and many similar changes take place. Most of these are due to the slow action of oxygen.

On *hot* substances of many kinds oxygen acts with great ease. A splinter of wood does not take fire in oxygen. But a glowing spark on the end of the splinter at once bursts into flame when the splinter is slipped into a tube of oxygen (Fig. 23). This is because the wood close to the spark is very hot, and the oxygen just around the spark has become hot. The two hot things combine very easily. The heat set free in this action raises the temperature of more and more wood and oxygen, and the burning continues with more and more vigor.

Substances that burn very slowly in air burn much more rapidly in pure oxygen, because more oxygen can get at them (air is only 21 per cent oxygen). In air, sulfur burns with a small, weak flame. In oxygen the flame is much larger and brighter (Fig. 57). Iron is hard to burn in air, but a fine wire, the end of which is heated to bright redness in air, will burn brilliantly in oxygen.

What have people believed about fire? We kindle a fire by striking a match, and do not stop to think that there must have been a time when men could not start a fire. No doubt primitive men were terrified by forest fires started by lightning long before they could start fires for themselves. It is not strange that many of them became fire-worshipers. The Greeks believed that Prometheus stole fire from the chariot of the sun and gave it to men. Slowly men learned to kindle fire by striking flints together, or by rubbing dry sticks one against the other; but no one knew what fire was. The phlogiston theory (p. 9) was the first real attempt to *account* for fire. After Priestley discovered oxygen, the French chemist Lavoisier (Fig. 58) felt sure this gas must have something to do with burning.

Lavoisier's great experiments. In place of merely speculating about fire, Lavoisier made *experiments.* This is the only way to find out the facts. He soon found that when iron or tin or lead is burned in a closed vessel filled with oxygen (or air), the metal increases in weight, and oxygen is used up. These experiments could mean only one thing: When a metal (or any element) burns, it combines with oxygen, and the product formed is a compound of the two elements. This discovery by Lavoisier, which proved the true nature of burning, was one of the greatest in the whole history of chemistry.

Many *compounds,* as well as elements, burn in oxygen. Usually the compound is decomposed, and each element in it burns separately to form a compound with the oxygen. Sometimes the compound unites with oxygen without being decomposed.

Let us imitate Lavoisier in an experiment. Let us put some very fine iron powder in a small porcelain dish *A* (Fig. 59) and counterpoise it on a balance, as shown in the figure. Now remove the dish from the balance and gently heat it until the iron begins to burn. After the glow stops, allow the dish to cool, and then put it back on the balance. The balance pan on which the dish rests at once sinks (Fig. 60), showing that the iron has increased in weight while being burned.

Does a burning candle increase in weight? If Lavoisier was right in his belief that the burning of any substance is due to the union of the substance (or of the elements that

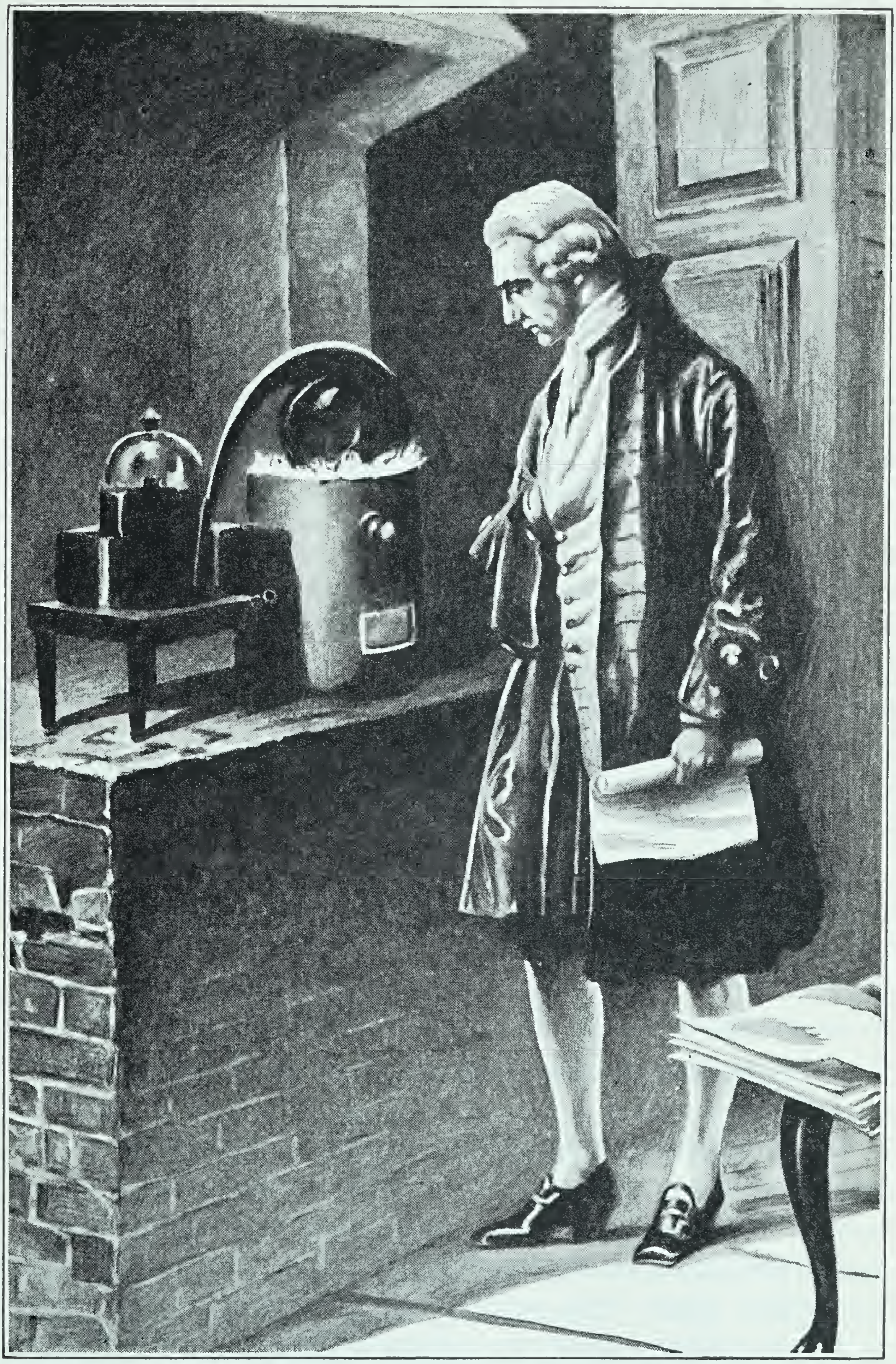


Fig. 58. Lavoisier (1743–1794)

The great French chemist, Antoine Laurent Lavoisier, the founder of modern chemistry, is here shown in his laboratory, conducting the famous experiments by which he proved the true nature of combustion. He was guillotined during the Reign of Terror because of his connection with the pre-Revolutionary government compose it) with oxygen, then the compound formed should weigh more than the original substance, because of the added oxygen. We have found this to be true in the case of iron. But how about a candle, which entirely disappears when it burns? Perhaps the compounds that are formed in the burning of the candle are invisible gases, and these pass off unnoticed. That this is true and that the gases that pass off weigh more than the part of the candle burned is shown in Fig. 61.

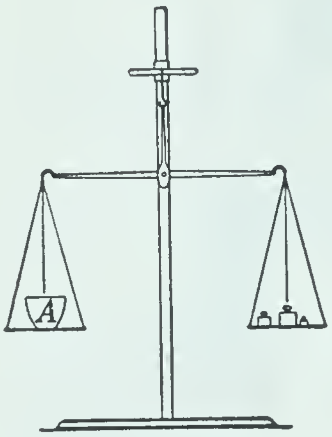


Fig. 59. A porcelain dish *A* containing very fine iron powder counterpoised on a balance

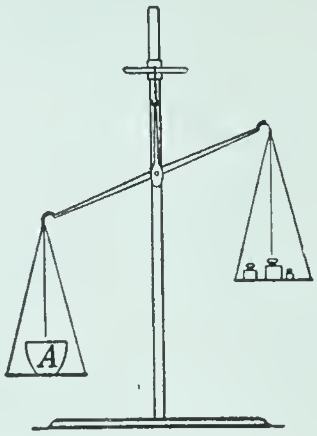


Fig. 60. After being heated in the air, the contents of the dish *A* are heavier than before

Some chemical terms: *oxidation* and *combustion*. When a substance combines with oxygen, we say that it is *oxidized* or that it undergoes *oxidation*. Later on we shall find that the term *oxidation* is used to describe a general group of reactions, even some in which oxygen takes no part. For the present, however, we shall use it in the sense just explained.

If oxidation takes place very slowly, no light is given off, and we notice no heat unless we make very careful measurements. The decay of wood and leaves and the rusting of metals are examples of this slow oxidation. But if the oxidation takes place very rapidly, the heat given off is very apparent and may cause the substance being oxidized to glow or even to burst into flame. We then say that the substance *burns* or undergoes *combustion*. Now substances often burn with a flame in other gases than oxygen; and two solids may become red-hot as they combine. The word *combustion* is used to describe all these cases, but the most familiar examples are combustion in oxygen. Combustion in air is similar to combustion in oxygen, since it is due to the oxygen in the air. For the present we may sum up the statements in this paragraph about oxidation and combustion as follows:

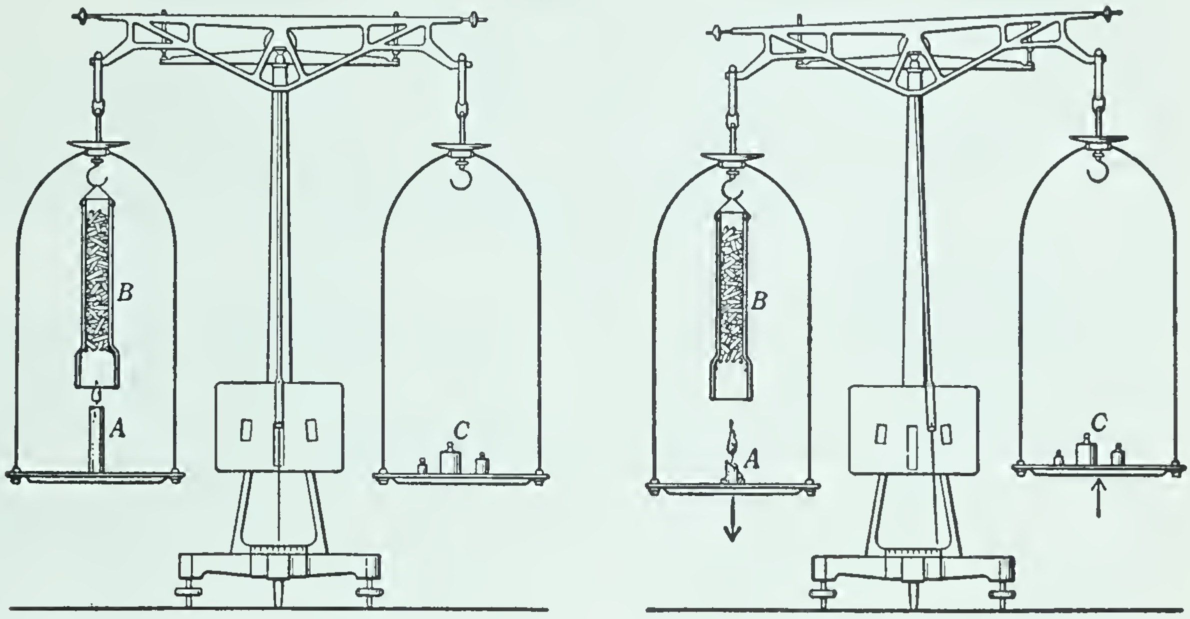


FIG. 61. The apparatus used to show that the gases formed by a burning candle weigh more than the burned part of the candle

A wide glass tube or lamp chimney B is loosely filled with pieces of caustic potash, a compound that absorbs the gases formed by the burning candle. The tube and contents are suspended above the candle A, as shown in the left-hand figure, and counterpoised by the weights C. The candle is then lighted. The hot gases formed by the burning candle rise in the tube and are absorbed by the caustic potash. As the candle burns, the pan upon which it rests slowly sinks, as shown in the right-hand figure. What does the experiment prove?

Oxidation is the action of oxygen on elements or compounds. Combustion is a chemical reaction giving off both light and heat.

Oxides, or compounds of elements with oxygen. The compound formed by the chemical union of any element with oxygen is called an *oxide* of that element. When burned in oxygen, iron forms an oxide of iron; sulfur, an oxide of sulfur. A candle is composed largely of compounds of carbon and hydrogen. When it burns, the carbon is oxidized to the oxide of carbon, called carbon dioxide (CO_2), while the hydrogen is oxidized to oxide of hydrogen (H_2O), which is the chemical name for water. All but about half a dozen elements form oxides; and most of them form more than one, so that there is a large number of oxides, many of which are found as minerals. Some are solid bodies, such as the oxides of iron and mercury. Others are liquids, water being the most familiar example. Quite a number are gases, such as the oxides of carbon and sulfur.

Products of oxidation; products of combustion. When any substance is oxidized, the compounds formed are called the *products of oxidation* of that substance. So, too, when a substance burns, the compounds formed are called its *products of combustion.* These are usually oxides, as we have seen to be true with iron and a candle.

The speed of combustion. We all know that the speed of a runner, or the time he makes, depends on quite a number of things: his physical condition, the state of the track, the weather. So, too, the speed of combustion of a substance — how fast it burns — depends on many factors, two of which should be very clear to us.

1. ***The speed depends on the temperature.*** Everyone knows that a lump of coal thrown into a hot furnace will burn faster than if put on freshly lighted kindling wood in the same furnace. This is because the hot furnace quickly raises the temperature of the coal, and at this higher temperature it burns faster. It is a general fact that *combustion goes faster the higher the temperature.* Oxidation that at ordinary temperatures takes years to make noticeable progress may be all over in no more than a few seconds at a very high temperature.

2. ***The extent of surface is important.*** A solid or a liquid can burn only at its surface. So the more oxygen we can bring into contact with the surface of the burning substance, the faster the combustion will go. The old-time blacksmith did this at his forge with his bellows.

Another way to do it is to increase the surface of the burning substance. A log of wood burns slowly. Cut the log into pieces and the speed of combustion increases, because of the larger surface of wood. Split the pieces into fine splinters and the combustion goes still faster. Grind the splinters into fine dust, and scatter the dust in the air, so that each particle of wood is surrounded by the oxygen in the air. If combustion is now started at some point by a spark or a flame, it will go so fast as to be nearly instantaneous, and a violent explosion will take place. In this way we are able to account

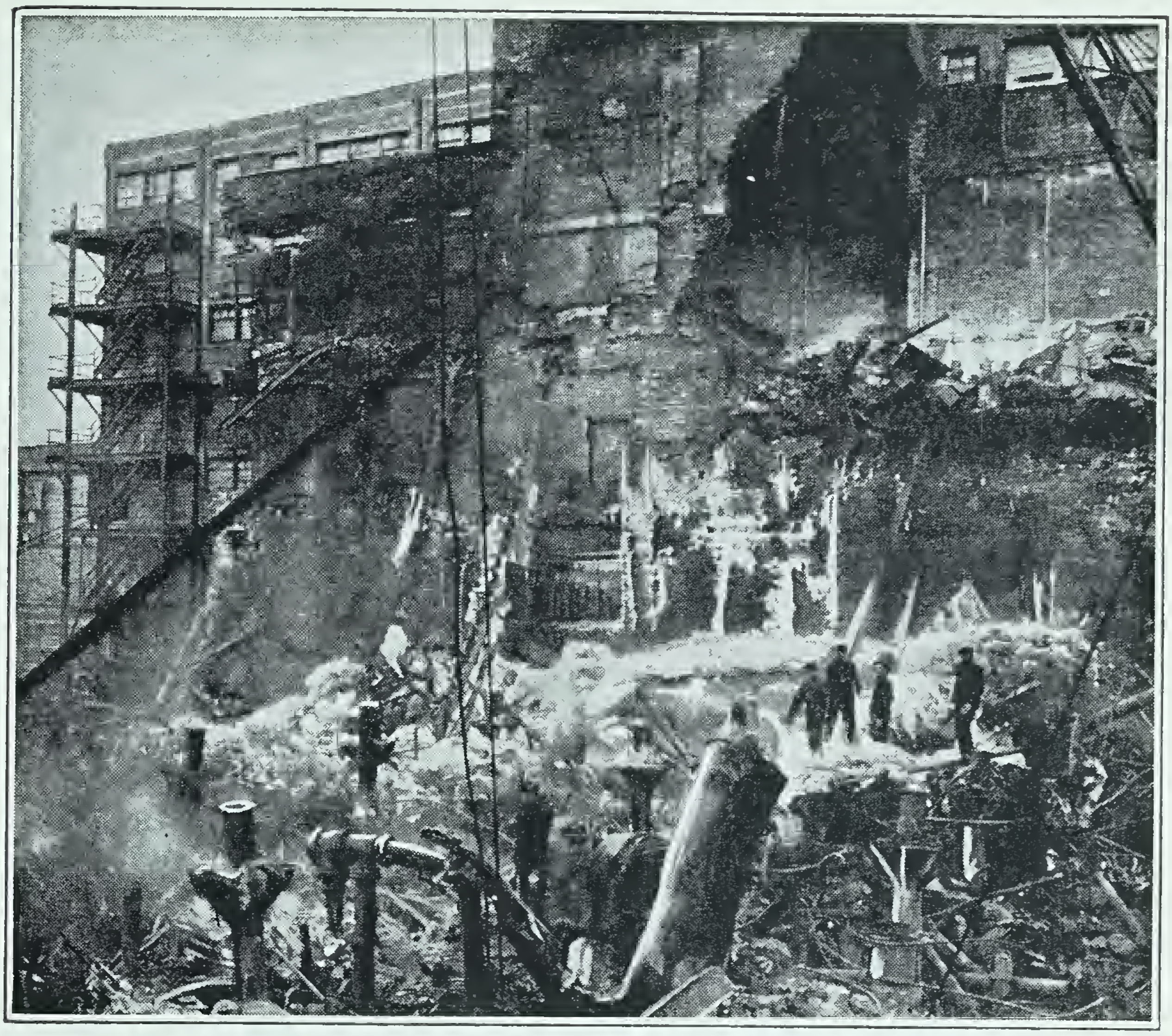


Fig. 62. Results of an explosion of starch dust in which forty-two men were killed and a large number seriously injured. What precautions would prevent such explosions?

Courtesy of the United States Bureau of Mines

for the many explosions in flour mills and starch factories (Fig. 62), and in other places where the air is thick with combustible dust.

Does the heat given off in a reaction depend on its speed? It is clear that a given substance may either oxidize slowly or burn rapidly. For example, a piece of phosphorus, lying in the air of a cool room, slowly wastes away until it has all been changed into a smoke consisting of particles of an oxide of phosphorus. But if the phosphorus is touched with a lighted match, it takes fire, burns very rapidly, and gives out much heat.

In both these cases the same thing is formed, namely, oxide of phosphorus. How about the heat? *Apparently* it is very different in quantity in the two reactions; but accurate experiment shows that it too is *exactly the same.* This seems strange; but when we know it is true, we can easily explain it. In the one case the reaction is so slow that the heat radiates away without our noticing it. In the other case the same amount of heat is given off very fast and is very evident to us. By experiment we know that this is true in all cases of oxidation.

The heat given off in the oxidation of a substance is exactly the same whether the reaction is fast or slow, provided the same compound is formed.

Spontaneous combustion, or fires that start themselves. Sometimes a fire starts itself, and the papers say, "It is a case of spontaneous combustion." We know this can happen, and we have little trouble in explaining it. We have seen that the speed of oxidation increases with the temperature (p. 90). Now suppose a slow oxidation starts, say in the middle of some hay in a barn. The heat given off is not carried away very easily, since the surrounding air is not moving. The spot in the hay grows hotter. This makes the oxidation go faster, throwing out more heat and making the spot still hotter. Suddenly the oxidation becomes an active combustion — a fire starts. Materials that take fire in this way are said to undergo *spontaneous combustion*. Certain oils, used in paints, are rather rapidly oxidized in air, and oily rags left by painters provide good conditions for spontaneous combustion. Many fires have been traced to this cause.

Kindling temperature. It is a well-known fact that substances will not start to burn unless heated to a certain temperature, which varies with the substance. We have seen that phosphorus is easily set on fire, while iron is difficult to ignite. The temperature to which any given substance must be heated in order for it to take fire and burn is called its *kindling temperature*.

What is oxygen good for? The most important use is the most evident one. We all know we must breathe oxygen or speedily die. Nature knows this so well that she has given us about six times the lung capacity we need, so that we can still go on living with a good deal of lung injury or disease or in thin air. All living things, except some very low orders of plants, must have oxygen.

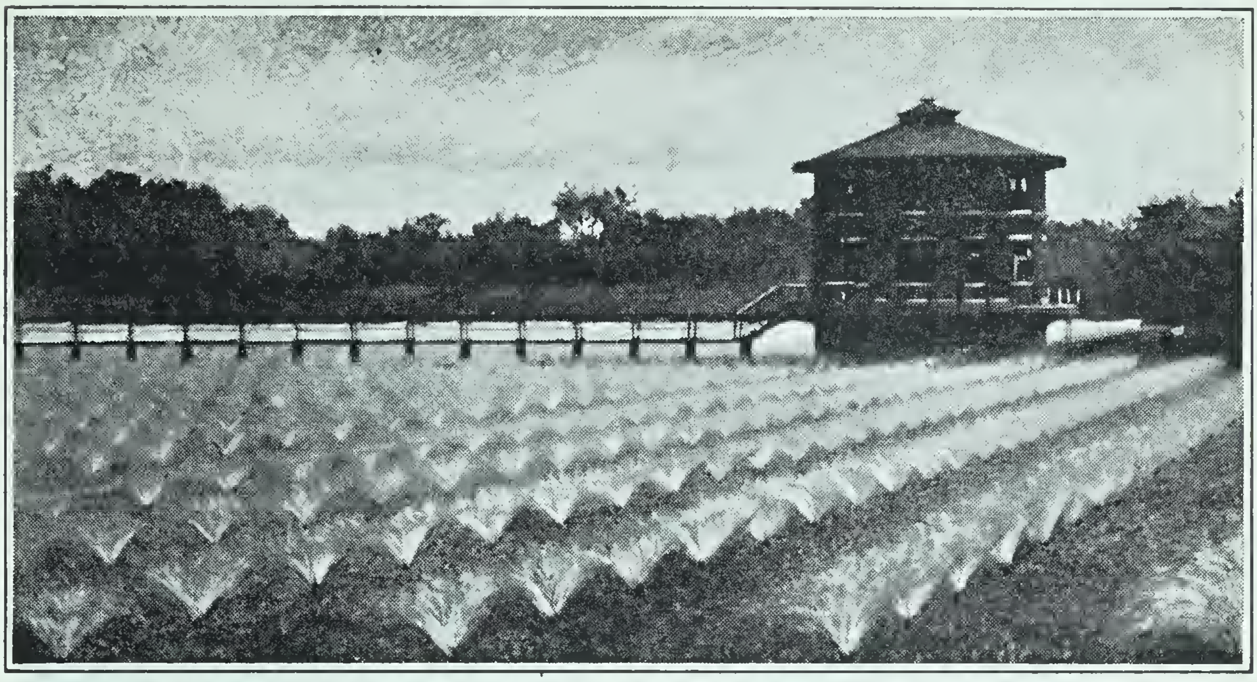


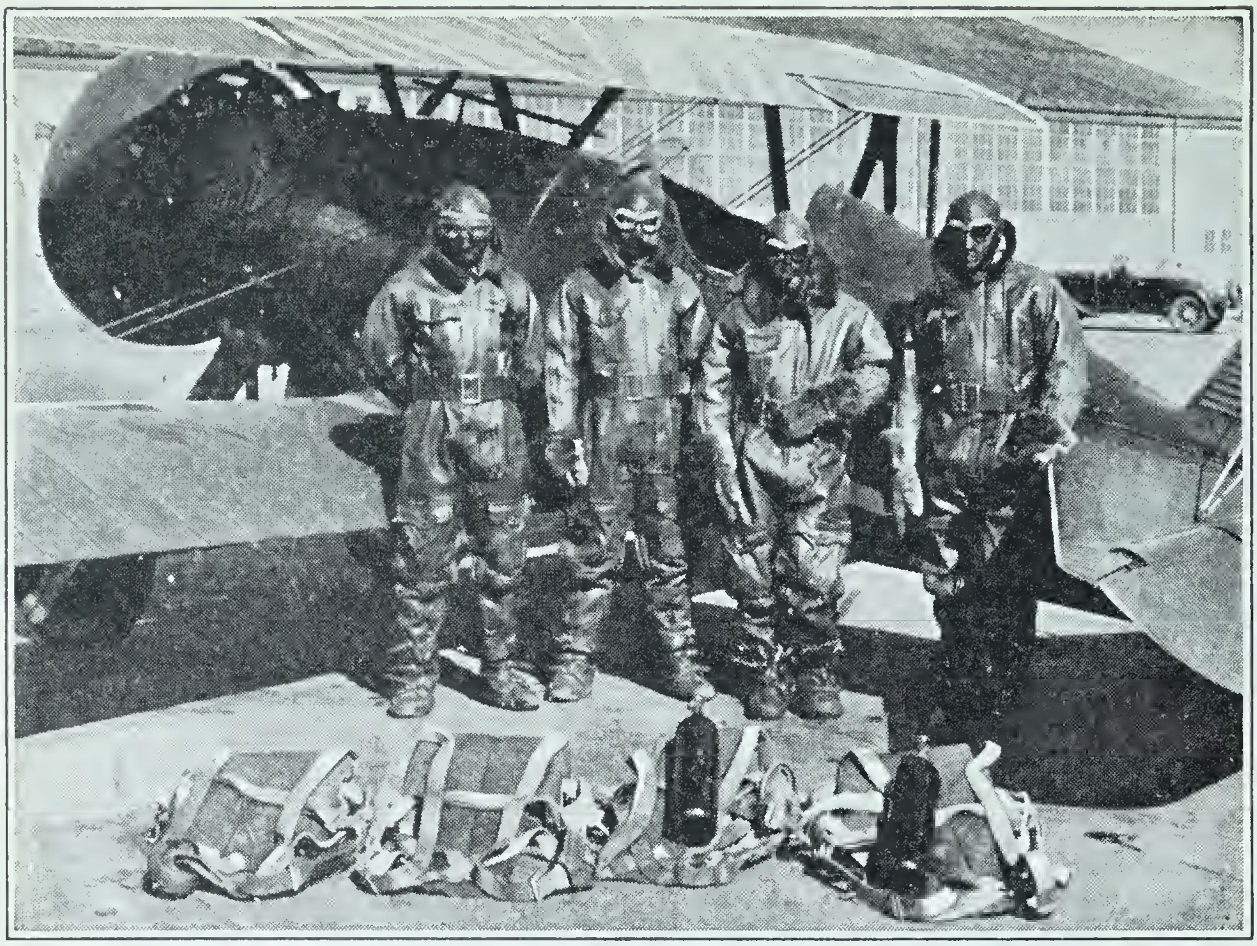
FIG. 63. View of a sewage-disposal plant, in which the sewage is sprayed into the air to secure its oxidation

Also, though it is not so evident, oxygen is necessary to life as a *purifying agent.* In some wonderful way certain *bacteria* (microscopic organisms) cause the oxygen of the air to oxidize the dead refuse of animal and vegetable life and so to change it into harmless substances.

For example, in the sewage-disposal plants of many cities, sewage is forced into the air in fine sprays (Fig. 63). This gives it a very large surface exposed to the oxygen of the air (p. 90), and as a result the decaying matter is rapidly oxidized. Were this not done, sewage would everywhere be a menace to health. Even the drinking water of some of our cities is partly purified by spraying in this way.

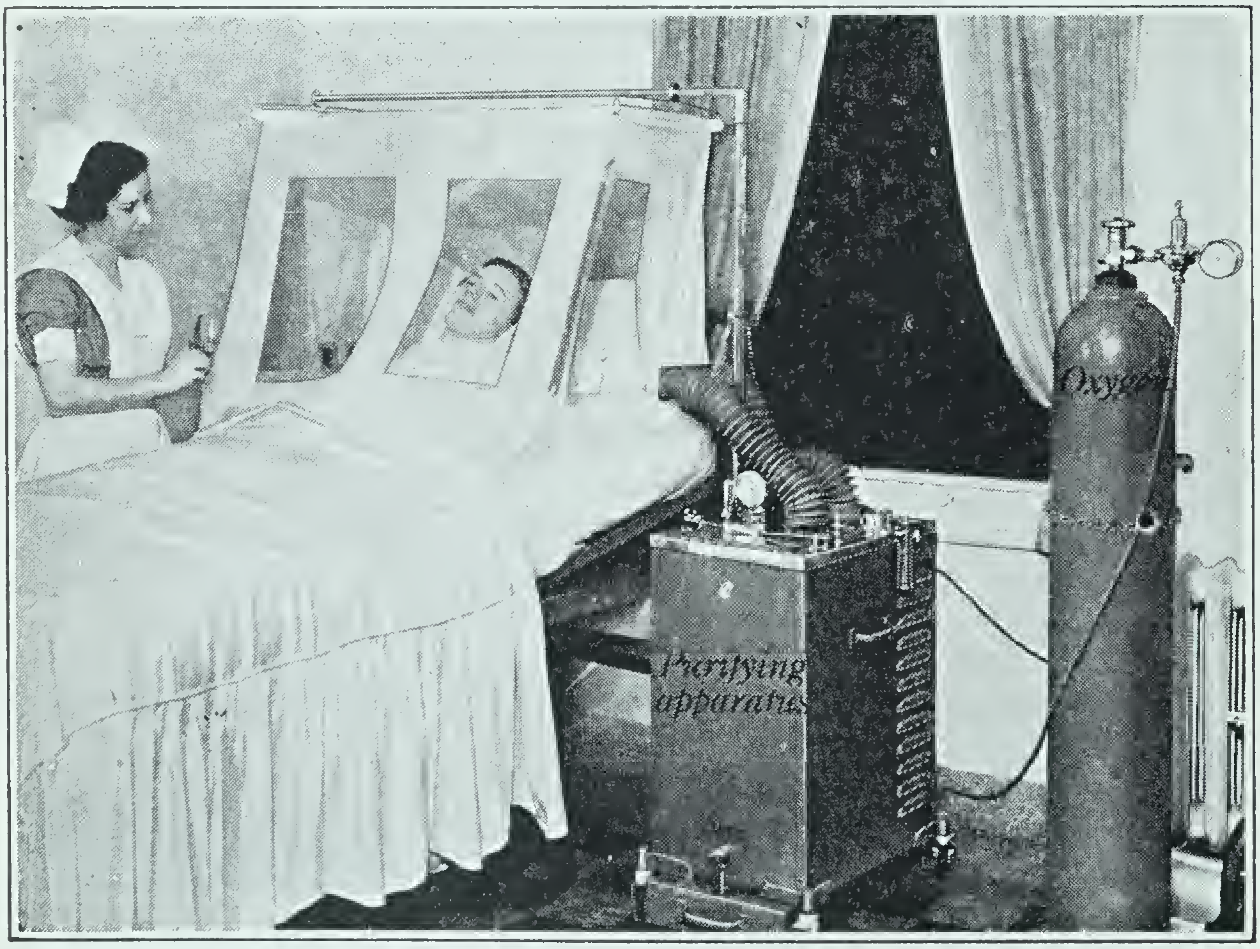
The greatest industrial use of pure oxygen is in getting high temperatures, as will be explained later. Enormous quantities of the gas are prepared annually from the air for this purpose. With these high temperatures we can do two things that seem the very opposite of each other: we cut to pieces large metal structures, such as old ships, and we weld together broken parts of machines.

Smaller quantities of oxygen are used in manufacturing useful compounds. Aviators are always supplied with pure oxygen for flights at high altitudes (Fig. 64), and miners use it in rescue work after explosions. In some diseases, such as pneumonia and tuberculosis, a portion of the lung is affected



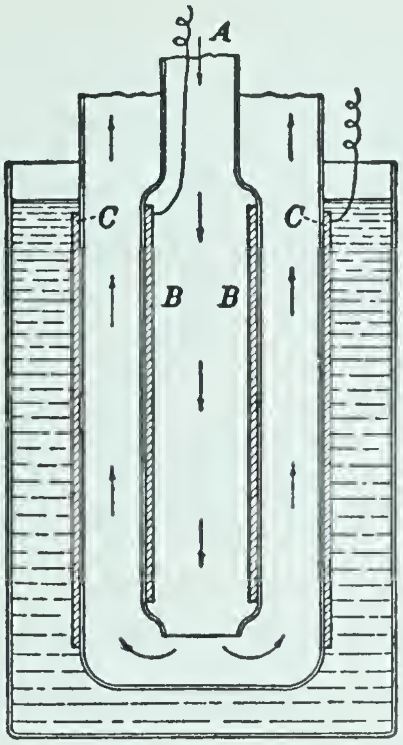
Official photograph, United States Army Air Corps

FIG. 64. Aviators ready for high-altitude flying. They are provided with helmets, face masks, and devices that supply oxygen if it is needed



McKesson Appliance Company

FIG. 65. Oxygen being administered to a patient ill with pneumonia



Oxygen enters at A, following the course indicated by the arrows. The metal surfaces B and C are separated by a space through which the oxygen passes. Wires from an induction coil are connected with B and C. As the oxygen passes upward between the metal plates it is acted upon by the electrical discharge, and a small percentage of the oxygen is changed into ozone

FIG. 66. A form of apparatus for converting oxygen into ozone

so that it cannot take its normal supply of oxygen. Such patients are often placed in an "oxygen tent" (Fig. 65), which is filled with air containing a larger percentage of oxygen than normal air contains.

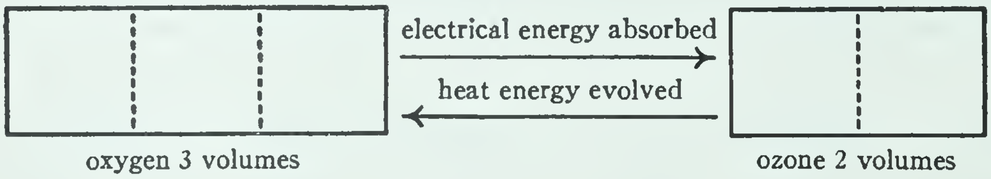
OZONE: A SECOND FORM OF OXYGEN

The odor near electrical machines. Everyone who has worked around electrical transformers or radio transmitters must have noticed the peculiar odor near such machines. Now an odor is always due to some gas that touches the sensitive nerves in our noses. What gas causes this odor? After years of experiment it was found that the odor is due to oxygen, *but oxygen in a new guise.* We call it *ozone,* from one of the Greek words meaning "smell." This double character of oxygen reminds us of an actor with one of whose roles we are very familiar, but who is suddenly found to have another, quite unsuspected.

How do we make ozone? In an electrical age it is easy to make ozone. It is only necessary to pass an electrical discharge through oxygen (or air) (Fig. 66). But the ozone easily changes back into oxygen even while we are making it.

So it soon comes about that the amount of oxygen changing into ozone is just equal to the amount of ozone changing back into oxygen. Then we can make no further progress. In scientific language we say that the oxygen and ozone are *in equilibrium with each other.* Usually this equilibrium is reached when about 5 per cent of the available oxygen has been changed into ozone, but much larger yields can be obtained at very low temperatures.

What do we know about ozone? The first thing we notice is that when oxygen changes into ozone there is a great change in its volume. *Three volumes of oxygen give only two volumes of ozone.* In the second place, it takes electrical energy to change oxygen into ozone, and when ozone changes back into oxygen an equivalent amount of heat energy is set free. These physical facts may be represented as follows:



The chemist has proved that each molecule of oxygen has *two* atoms of oxygen (p. 33), while the molecule of ozone has *three.* So he represents the relation of the two substances by the following equation, which tells us that three molecules of oxygen form two molecules of ozone and vice versa.

$$3\,O_2 \rightleftharpoons 2\,O_3$$

The double arrows indicate that the reaction may go in either direction and that an equilibrium will be reached.

Conduct and uses. Pure ozone is a pale-blue gas, 1.5 times as heavy as oxygen. As one might expect from its composition, it is a very powerful oxidizing agent — much more so than oxygen. But few uses have been found for it, and these all depend upon its oxidizing properties.

Ozone in the air. Every flash of lightning through the air must change some oxygen into ozone; yet we can rarely find any traces of it. Ozone is far too active chemically to last long in an atmosphere full of dust particles of all kinds, many of which are easily oxidized. High up in the atmosphere there seems to be a region rich in ozone, and this has an important effect on the quality of our sunlight and probably on radio transmission. Some scientists insist that if it were not for this layer of ozone, life would be impossible; for the particular rays absorbed by the ozone are destructive to living cells.

Allotropic forms of elements. Oxygen and ozone are not the only example of two distinct forms of the same element. Indeed, we shall find that most of the elements occur in two or more forms that are as strikingly different as are oxygen and ozone. In scientific words, chemists call these the *allotropic forms* of elements. Their difference in properties is due chiefly to their difference in energy content.

An element (or a compound) that occurs in two or more forms that differ in properties because of differences in chemical energy is said to occur in allotropic forms.

CHAPTER SUMMARY IN QUESTION FORM

NOTE. It is important for the student to keep in mind that, unless otherwise stated, when the volume of a gas is referred to in the text it means the volume of the gas measured under standard conditions. The student should also remember that the weight of 1 liter of each of the common gases, measured under standard conditions, is given in a table facing the inside of the back cover.

1. When and by whom was oxygen discovered?

2. (*a*) From what compound was oxygen first obtained? (*b*) By what means was the oxygen liberated from this compound?

3. (*a*) Where do we find oxygen in the free state? (*b*) in the combined state?

4. Explain how you can obtain oxygen from (*a*) mercuric oxide; (*b*) water; (*c*) potassium chlorate.

5. What is the source of the oxygen sold on the market?

6. In the laboratory method for obtaining oxygen, does the oxygen come from the potassium chlorate or the manganese dioxide or both?

7. What name do we give to a substance that aids chemical action yet remains unchanged at the end of the action?

8. (*a*) What questions do we answer in naming the physical properties of an element? (*b*) Answer these questions in reference to oxygen.

9. (*a*) What questions do we answer in describing the chemical conduct of an element? (*b*) Answer these questions in reference to oxygen.

10. (*a*) How did the chemists of the eighteenth century explain burning? (See phlogiston, p. 9.) (*b*) Who first gave the true explanation of burning?

11. State the change that takes place (*a*) when an element burns; (*b*) when a compound burns.

12. Describe Lavoisier's experiments by which he proved the true nature of burning.

13. Matter cannot be destroyed; yet a candle entirely disappears in burning. Explain.

14. How does the weight of a candle compare with the weight of the products formed when it burns?

15. Define the following terms: (*a*) oxidation; (*b*) combustion.

16. (*a*) What is an oxide? (*b*) Describe the oxides as a group.

17. (*a*) Mention two ways by which you can make a substance burn more rapidly, and (*b*) give an example of each.

18. What is meant by the following terms: (*a*) products of oxidation? (*b*) products of combustion?

19. Does it make any difference in the amount of heat set free whether a substance such as a log of wood or a lump of coal burns slowly or rapidly?

20. What kind of combustion is said to occur when a substance takes fire without being lighted? How do we account for such fires?

21. Explain the meaning of each of the following terms: (*a*) kindling temperature; (*b*) spontaneous combustion; (*c*) heat of oxidation.

22. Give five different uses of oxygen.

23. Which weighs the more, 1 liter of oxygen or 1 liter of air?

24. (*a*) What name do we give to the substance formed when an electrical discharge is passed through oxygen? (*b*) Mention three ways in which this substance differs from oxygen. (*c*) How do we account for this difference in the properties?

25. Some elements occur in two or more forms, which differ more or less in their properties. What name do we give to such forms?

THOUGHT QUESTIONS

1. (*a*) Describe the physical appearance of each of three compounds from which oxygen can be prepared. (*b*) Can you tell from their looks that they contain oxygen? (*c*) Which contains the largest percentage of oxygen?

2. Give two reasons for painting houses and metal structures, such as iron bridges.

3. State the chemical changes that take place in preparing oxygen from each of the following compounds: (*a*) mercuric oxide; (*b*) water; (*c*) potassium chlorate. (*d*) What product other than oxygen is obtained in each case?

4. We often say that we *make* oxygen in the laboratory. (*a*) Is this statement strictly true? (*b*) Explain.

5. Name two kinds of energy used in liberating oxygen from its compounds.

6. Suppose that oxygen were very soluble in water. How could you collect it?

7. Oxygen has no odor, and sulfur a very faint one. How do you account for the very marked odor that always accompanies the burning of sulfur in oxygen?

8. When a candle burns we get water and carbon dioxide. (*a*) Where do these two compounds come from? (*b*) What does their formation prove?

9. Criticize the phlogiston theory of combustion.

10. Many of us use gas in our homes with perfect safety for heating, cooking, and lighting. Yet we sometimes read of houses being blown to pieces by gas explosions. How do you account for such explosions?

11. How does the use of kindling help us to start a fire?

12. (*a*) Is the giving off of light a sure proof of combustion? (*b*) If not, give examples.

13. Explain why it is that you blow a candle flame to put out the flame but blow a glowing coal to start the flame.

14. (*a*) Is combustion always a process of oxidation? (*b*) Is oxidation always a process of combustion?

15. Which of the following statements are true and which false? (*a*) Oxygen can be prepared by heating any compound that contains it. (*b*) Oxygen combines with all the elements. (*c*) The compound formed when oxygen combines with another element is an oxide. (*d*) When potassium chlorate is heated, the combined weights of the resulting potassium chloride and oxygen equal the weight of the potassium chlorate decomposed. (*e*) Oxygen is necessary for combustion. (*f*) Oxygen is necessary for producing light.

16. Why do we say that oxygen is a gas when it can be obtained in both the liquid and the solid form?

OPTIONAL EXERCISES

1. Suggest different methods for putting out fires, and explain how each would act.

2. Three students prepared oxygen. Student A decomposed 100 g of water by electrolysis. Student B heated 100 g of mercuric oxide. Student C heated 100 g of potassium chlorate mixed with 10 g of manganese dioxide. (*a*) Which student obtained the greatest weight of oxygen? (*b*) What weight did he obtain? (*c*) What volume?

3. (*a*) One hundred grams of water contains how many grams of oxygen? (*b*) Calculate the volume of this weight of pure oxygen.

4. What weight of potassium chlorate is required to prepare 100 liters of oxygen?

5. Write a brief biographical sketch of any one of the great chemists mentioned in this chapter.

CHAPTER VIII

Hydrogen

[The Lightest of All Elements]

Of what use is hydrogen to us? People in general are not so familiar with hydrogen as with oxygen. They may know that it is a very light gas and may have heard that it is used in inflating balloons and the great Zeppelins that in recent years have made regular trips across the ocean. While hydrogen is well suited for this purpose because of its lightness, it is very inflammable, and so is a constant source of danger. Many of you will recall the destruction of the great Zeppelin the *Hindenburg* (Fig. 67), in 1937, due to the fact that in some way the hydrogen with which it was inflated caught fire.

In the United States we use the noncombustible gas helium for inflating our dirigibles, as will be described in a later chapter. It seems probable that we shall have a sufficient supply of this gas so that we may share it with other nations. The use of hydrogen for this purpose, then, is largely a thing of the past, but is of historical interest.

But hydrogen has many other uses. Later on we shall find that large quantities of the element are used in changing some kinds of oils into solid fats and so making them more useful for many purposes. It is also used in the manufacture of valuable fertilizers and of compounds of the greatest importance in the industries. Hydrogen is also one of the chief constituents of a number of fuel gases, such as coal gas and water gas. We might call it the farmer's friend and the cook's assistant.

Where do we find hydrogen? There is not nearly as much hydrogen in the world as oxygen. Only very small amounts are found in the free state — mere traces in the atmosphere; consequently we have to get it from its compounds. Water (and, of course, all things that have water in them) contains hydrogen. Petroleum and natural gas are mixtures of many compounds nearly all of which are compounds of hydrogen with carbon. If we were able to live on the surface of the sun,

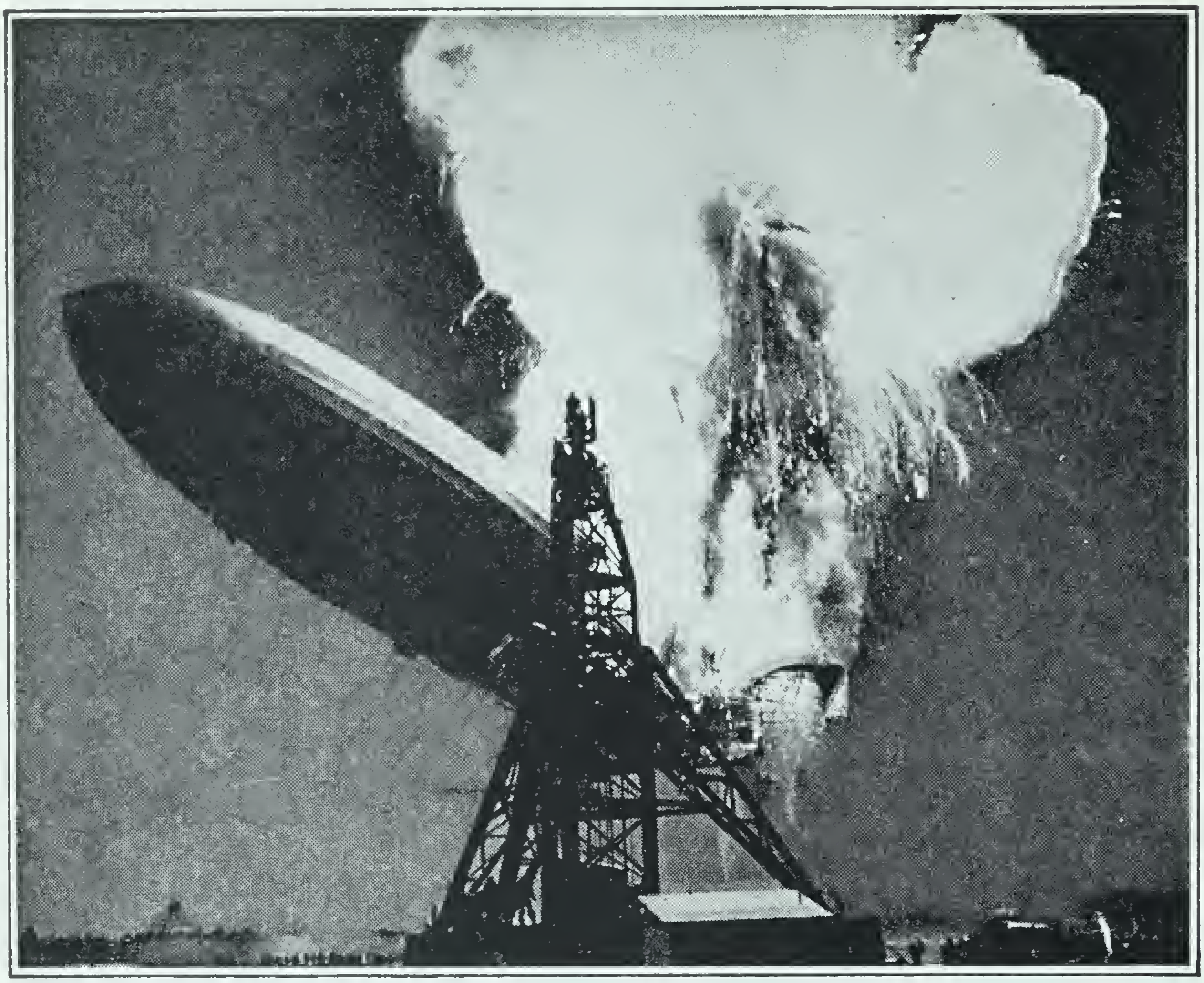


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Fig. 67. The photograph shows one of the uses of hydrogen, as well as the danger attending its use

The passenger airship *Hindenburg*, after making ten round trips between Germany and the United States during the summer of 1936, took fire as it was landing at Lakehurst, New Jersey, May 6, 1937, on its first trip of the year. The figure shows the flame of the burning hydrogen

we could get hydrogen from the atmosphere just as we get oxygen on earth; for there are vast quantities of hydrogen in the sun's atmosphere.

Cavendish, the discoverer of hydrogen. The early chemists were familiar with a few of the liquids we call acids. They knew that if these acids were poured on such metals as iron or zinc, bubbles of gas were formed on the metal and rose through the liquid. At the time Priestley was experimenting so successfully with his "airs" (p. 79), another Englishman, Henry Cavendish (Fig. 68), repeated the experiments of the older chemists. But he did more than look at these bubbles. He collected some of the gas that formed them, and made a study of it. In 1766 he got some of it in a pure state and proved it to be different from any known gas. Cavendish called it *inflammable air*, because it burns so easily. Later

Lavoisier renamed it *hydrogen*, a name derived from a Greek word meaning "producer of water." It is a good name; for when hydrogen burns, water is formed — a fact first discovered by Cavendish. Yet neither Cavendish nor Priestley ever gave up the theory of phlogiston, or accepted Lavoisier's proof of the nature of combustion!

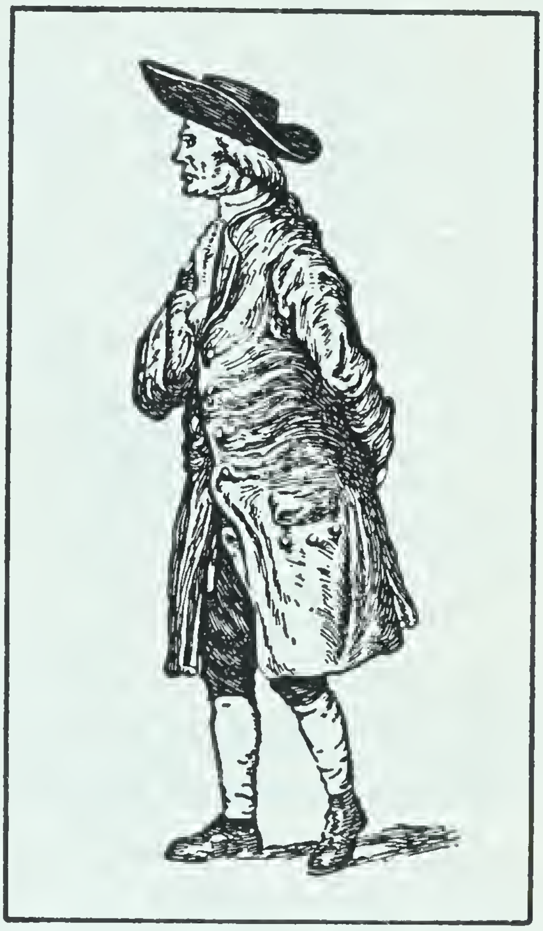


Fig. 68. Henry Cavendish (1731–1810)

A famous English scientist, contemporary with Joseph Priestley. He described hydrogen as a new gas, and showed that it produced water when burned

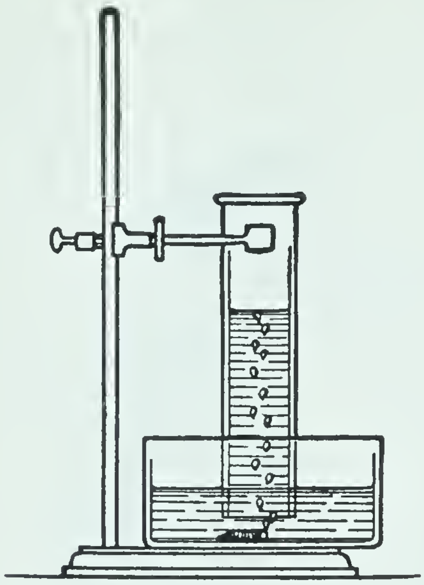
Getting a supply of hydrogen. The only way we can get hydrogen is from some of its compounds. We naturally use those which give us hydrogen most easily. Water and acids give us the best results.

1. ***Hydrogen from water.*** We can get hydrogen from water in two general ways: (*a*) We may electrolyze the water, as already described (Fig. 55), and so obtain both hydrogen and oxygen. This way is more useful in the industries than in the laboratory. (*b*) We may act on water with certain of the metals that combine with the oxygen of the water and set free a part or all of its hydrogen.

A few of the metals act rapidly on water at ordinary temperatures. For example, if we drop a small piece of the metal *sodium* on water, a lively reaction takes place at once. Enough heat is set free to melt the sodium, which runs about on the surface of the water in small silvery drops. In this reaction sodium takes the place of *half* of the hydrogen of the water, and we may represent the reaction in the equation

$$\underset{\text{sodium}}{2\,\mathrm{Na}} + \underset{\text{water }(\mathrm{H_2O})}{2\,\mathrm{HOH}} \longrightarrow \underset{\text{hydrogen}}{\mathrm{H_2}} + \underset{\substack{\text{sodium}\\\text{hydroxide}}}{2\,\mathrm{NaOH}}$$

The compound sodium hydroxide formed in the reaction is dissolved in the excess of water present, and can be obtained



Since the sodium is lighter than water, it is kept under the water by pushing a pellet of the metal into one end of a short piece of lead or tin pipe, the other end of which has been hammered flat. The pipe containing the sodium is then dropped into water, and a cylinder or bottle entirely filled with water is suspended over it. The hydrogen is at once evolved, and collects in the cylinder as shown in the figure

Fig. 69. Preparation of hydrogen by the action of sodium on water

as a white solid by boiling off all the water. The hydrogen, being but slightly soluble in water, may be collected over water as shown in Fig. 69.

Other metals, such as *magnesium* and *iron*, decompose water very rapidly, but only at a higher temperature. If we use iron, we must heat it red-hot and pass steam over it (Fig. 70). The iron combines with the oxygen of the steam, forming iron oxide and setting free *all* the hydrogen as a gas.

2. ***Hydrogen from acids — a good laboratory method.*** The *acids* are a very important class of compounds, and they will take a great deal of our attention in later chapters. What we need to know now is that they all contain hydrogen, and that some of them act on certain metals in such a way as to give up their hydrogen. The arrangement of a simple apparatus for getting hydrogen in this way is shown in Fig. 71.

In practice it has been found cheapest and most convenient to use either zinc or iron as the metal, with either *hydrochloric acid* or *sulfuric acid* as the acid. Hydrochloric acid is a water solution of a soluble gas called hydrogen chloride. This gaseous compound has the formula HCl, and is composed of 2.77 per cent hydrogen and 97.23 per cent chlorine. Sulfuric acid is a solution (in water) of an oily liquid called hydrogen sulfate (H_2SO_4). This compound is made up of 2.05 per cent hydrogen, 32.70 per cent sulfur, and 65.25 per cent oxygen.

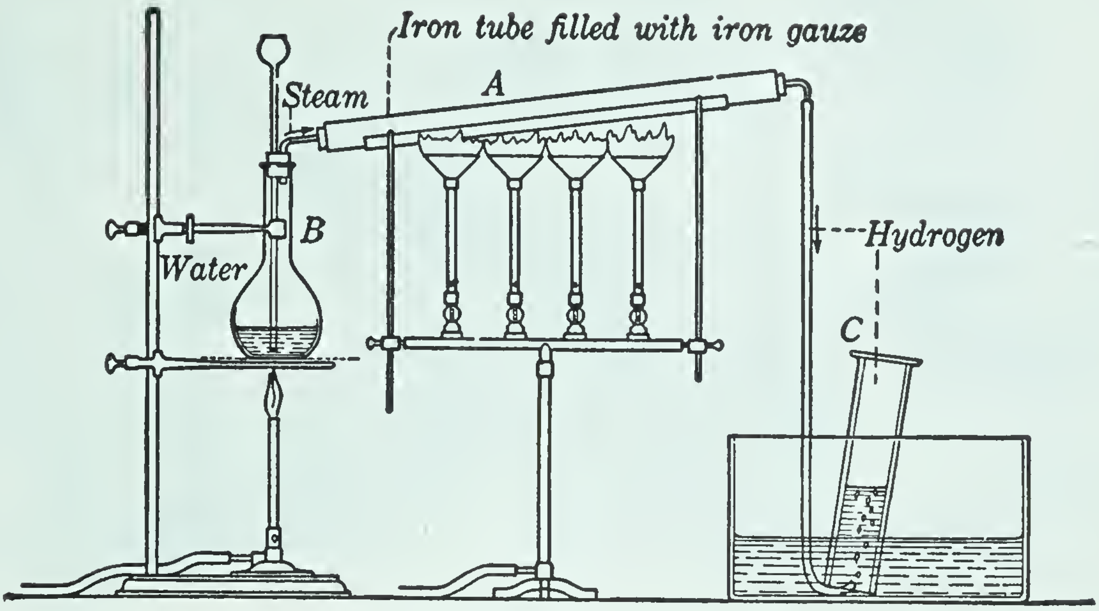

Iron tube filled with iron gauze
Steam
A
B
Water
Hydrogen
C

Fig. 70. The preparation of hydrogen by passing steam over hot iron

The steam, generated by heating the water in flask *B*, passes through the tube *A*, which is filled with hot iron gauze. The oxygen in the steam combines with the hot iron, thus liberating the hydrogen. The hydrogen passes on and is collected over water in the cylinder *C*

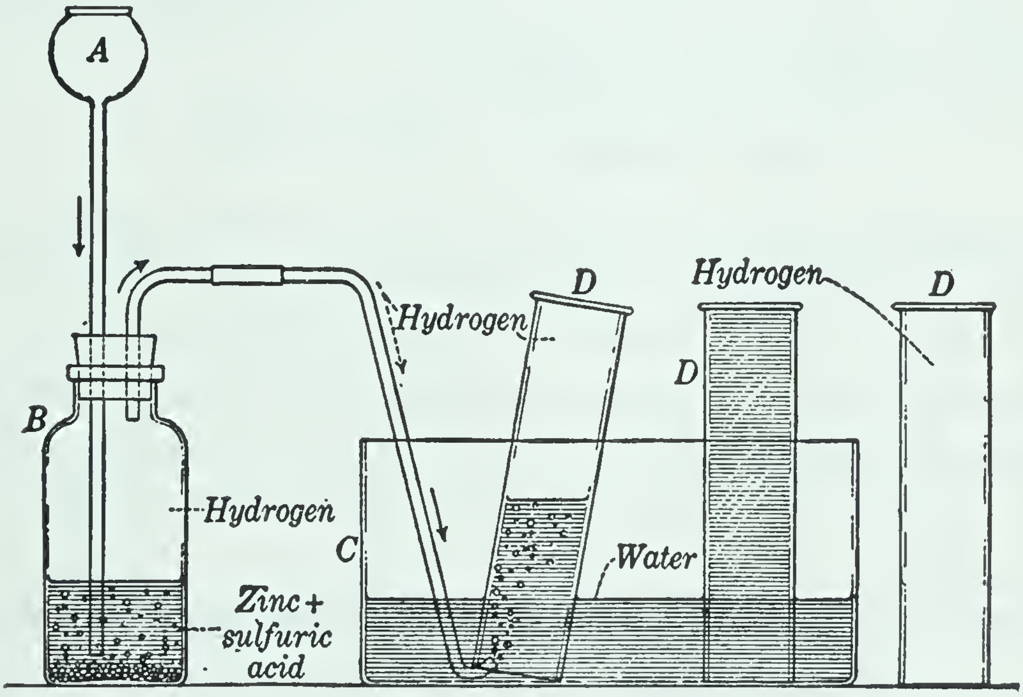

A
D
Hydrogen
D
Hydrogen
D
B
Hydrogen
C
Water
Zinc + sulfuric acid

Fig. 71. The preparation of hydrogen from acids

The metal (zinc or iron) is placed in the bottle *B*, and the acid (dilute sulfuric or hydrochloric) is added slowly through the funnel tube *A*. The metal displaces the hydrogen in the acid. The hydrogen thus liberated escapes through the exit tube and is collected over water in the jars *D, D, D*. Why does the end of the funnel tube *A* extend below the liquid in *B*?

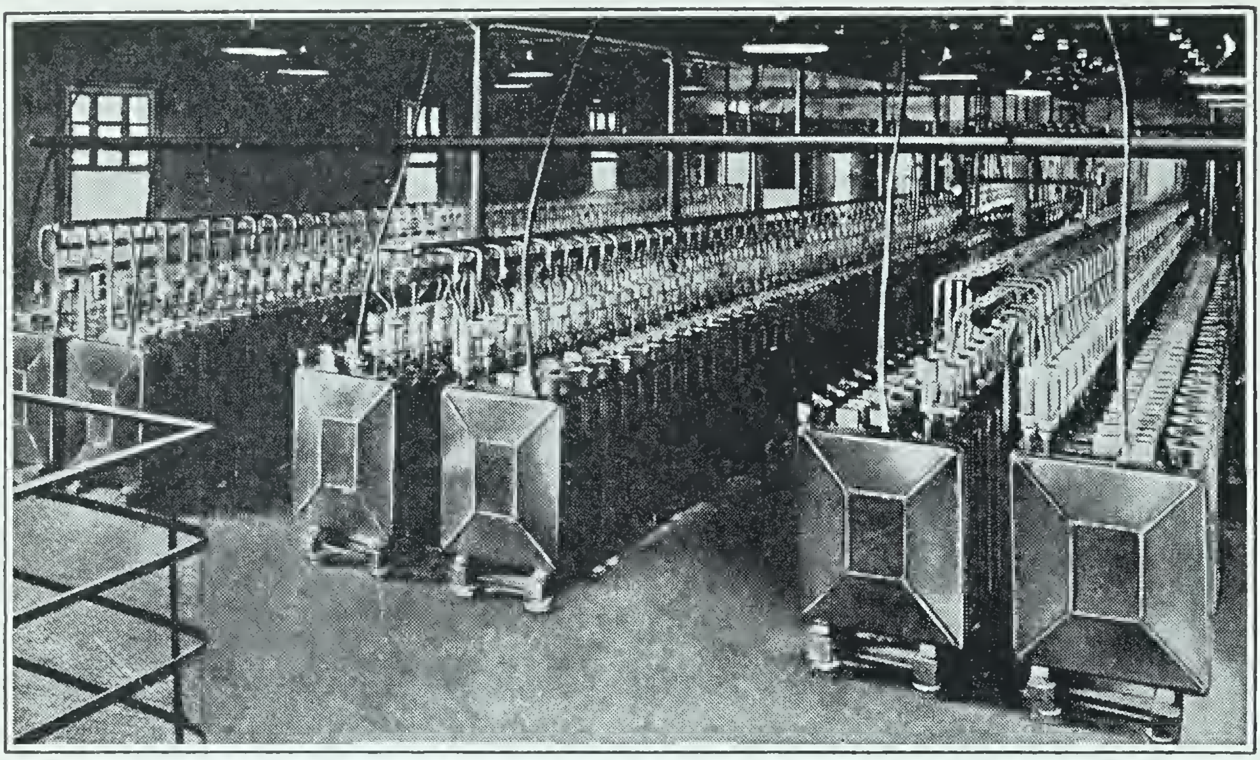


Fig. 72. View in a plant for the commercial production of hydrogen and oxygen by the electrolysis of water

The apparatus consists of a series of connected cells. The tubes shown leading from each of the cells are so arranged as to conduct away the hydrogen and oxygen in separate tubes. (Courtesy of the Gas Industries Co.)

If we use zinc and sulfuric acid, the hydrogen is liberated as shown in the following equation:

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

This equation tells us that the zinc takes the place of the hydrogen in the acid, forming the compound $ZnSO_4$ (called zinc sulfate). The hydrogen set free is collected over water as shown in Fig. 71. The zinc sulfate formed is a white solid, and remains dissolved in the excess of water in the acid. It may be obtained by boiling off the water after the metal has all dissolved.

Laboratory methods contrasted with commercial methods. When we wish to prepare small quantities of any element or compound in the laboratory, we use methods that need only simple apparatus. When we wish to prepare them on a large scale for commercial purposes, then we must use the cheapest methods. So it often happens that the commercial methods and the laboratory methods are different.

A number of commercial methods are used for getting hydrogen. Sometimes it is prepared by the electrolysis of water (Fig. 72), but the method most largely used is the action of hot carbon on steam. While the reaction takes place in steps, and is rather complicated, requiring the use of catalysts, we may represent it in a general way as follows:

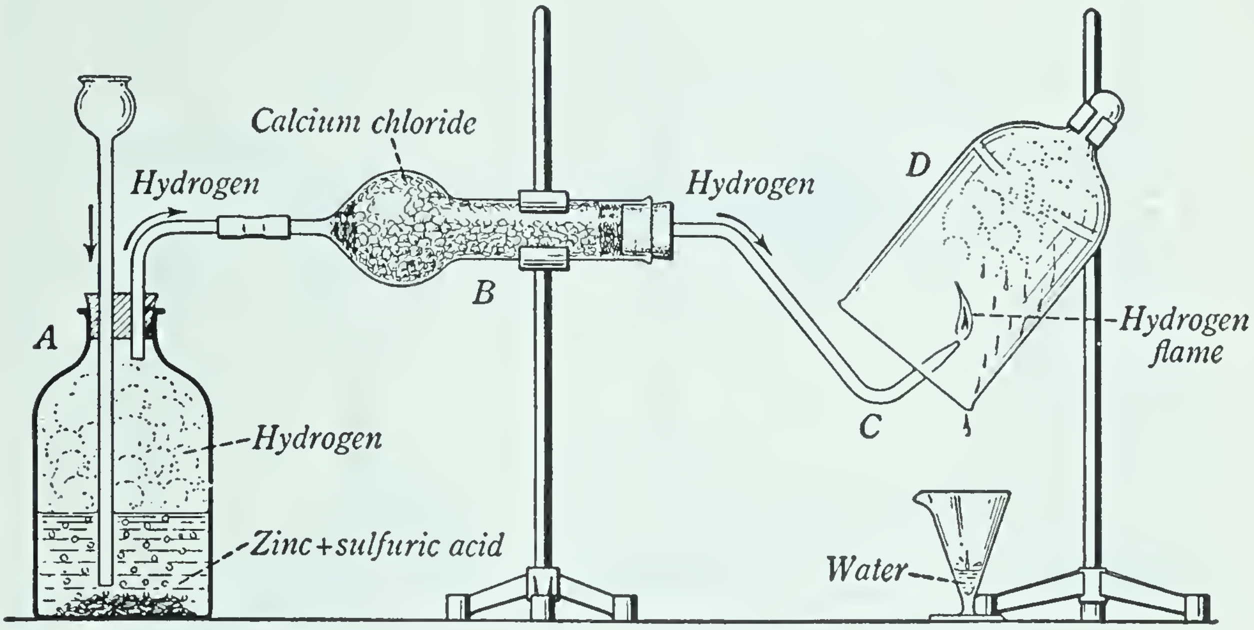


FIG. 73. Burning hydrogen in air and collecting the product of its combustion (water)

The hydrogen is generated in the bottle A, and is dried by conducting it through the tube B, filled with calcium chloride (which has a great attraction for moisture), and escapes through the tube C, which is drawn out to a jet as shown in the figure. *When all the air has been expelled from the apparatus*, the hydrogen is ignited. It then burns quietly, since only the small amount of it which escapes from the jet at any one moment can come into contact with the oxygen of the air. By holding a cold, dry bell jar D over the flame as shown in the figure, the steam formed by the combustion of the hydrogen is condensed. If the jar is kept cold and enough hydrogen is burned, water collects in drops and falls into the glass

$$2\,H_2O + C \longrightarrow CO_2 + 2\,H_2$$

The gas, carbon dioxide, formed along with the hydrogen is soluble in water, and so can be separated easily from the hydrogen.

A description of hydrogen — its physical properties. Like oxygen, hydrogen is a gas without any color, taste, or odor. It is only about half as soluble in water as is oxygen. The most striking thing about it is its extreme lightness. One liter of it weighs only 0.08987 g, or in round numbers 0.09 g, while 1 liter of air weighs 1.2930 g. Hydrogen is not poisonous, but of course we could not live in an atmosphere of it.

How hydrogen acts — its chemical conduct. The most interesting thing about the conduct of hydrogen is its affinity for oxygen. It not only combines with free oxygen but reacts with many of its compounds, especially the oxides, and takes away their oxygen. The product formed in either case is always water (H_2O). Aside from oxygen not many

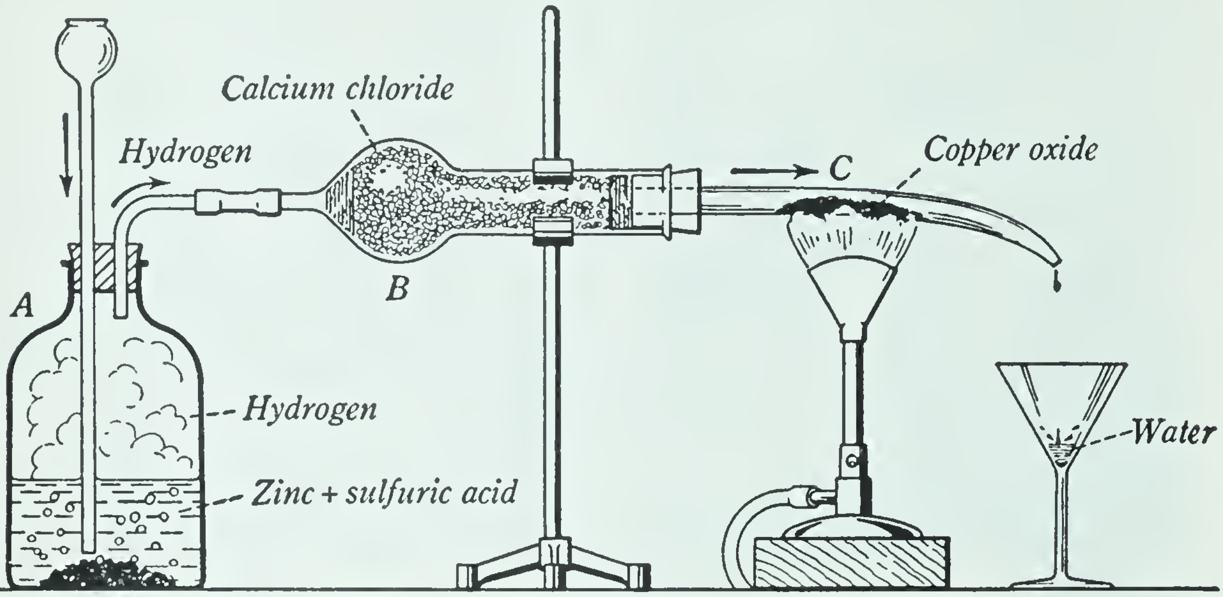


FIG. 74. The reduction of hot copper oxide by a stream of hydrogen. Why is it necessary to pass the hydrogen through the tube *B*?

elements combine directly with hydrogen, and we often have to employ pressure, heat, or a catalyst (or all three) to make the two combine. Although petroleum is made up largely of compounds of hydrogen and carbon, it is very difficult to make these two elements combine directly. Evidently nature has used some trick here that we find very hard to repeat in the laboratory.

The union of hydrogen with free oxygen. At ordinary temperatures these two gases can be mixed together without any reaction taking place. But if an electric spark or a flame comes into contact with the mixture, the two gases combine with explosive force. Their chemical energy is changed into a great deal of heat, which is set free in the reaction.

Still, we can devise ways of making the two gases combine without an explosion. This is best done by burning a stream of hydrogen from a jet directed into an atmosphere of oxygen (or air) as shown and described in Fig. 73. The flame of the burning hydrogen is not like most flames, since it is nearly invisible as well as very hot.

The action of hydrogen upon oxides. This action may best be shown by means of an experiment. A stream of hydrogen is generated in the bottle *A* (Fig. 74) and is dried as it passes through the tube *B*, which is filled with calcium chloride, a compound that has a strong affinity for water and so removes all water vapor from the hydrogen. The dry hydrogen is now led through the tube *C*, which contains a few grams of copper oxide (CuO), heated to a moderate temperature. The hydrogen takes away the oxygen from the copper oxide, forming water and setting the copper free, as shown in the following equation:

$$CuO + H_2 \longrightarrow Cu + H_2O$$

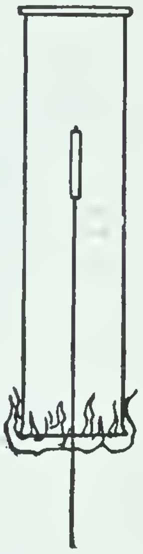


FIG. 75. Candle flame put out by hydrogen

As the reaction takes place the black color of the copper oxide gradually gives place to the red color of the copper, while the water formed drops from the end of the tube *C* into the glass. In this experiment the copper oxide is said to be *reduced*, and the process is called *reduction*. While the copper oxide is reduced in this experiment, the hydrogen is oxidized. It is always true that when one substance is reduced another is oxidized. Later on we shall see that *reduction*, like *oxidation*, is used in a broader sense.

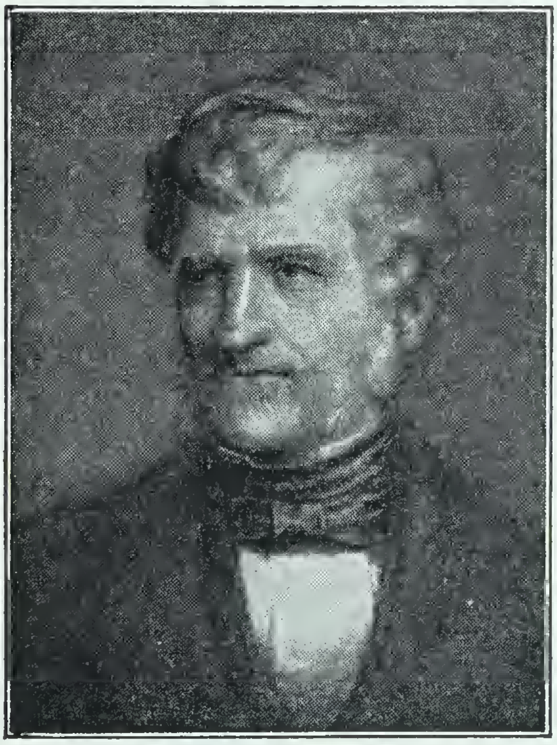


FIG. 76. Robert Hare (1781–1858)

An early American chemist, who invented the oxyhydrogen blowpipe

Hydrogen does not support combustion. By this we mean that those materials that burn in oxygen or in air will not burn in an atmosphere of hydrogen. For example, we all know that a candle will burn in air. But if we fill a bottle or a glass cylinder with hydrogen (Fig. 75) and slowly push a lighted candle (attached to the end of a wire) into the hydrogen, the candle flame goes out. But before it is extinguished, it sets fire to the hydrogen at the mouth of the cylinder, which burns in the oxygen of the air to form water. If we slowly withdraw the candle from the cylinder, it is lighted again as it passes into the air through the layer of burning hydrogen.

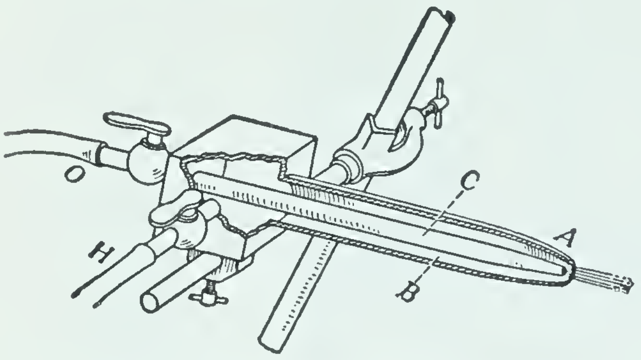


FIG. 77. The oxyhydrogen blowpipe

Chemical agents. An agent is one who brings about some sort of transaction, or who tries to do so. A chemical agent (or reagent) is a substance that brings about some sort of chemical reaction. If this agent brings about a reduction, it is called a *reducing agent*; in a similar way, if it brings about oxidation (p. 88), it is called an *oxidizing agent.*

The oxyhydrogen blowpipe. This apparatus, devised for giving a very hot flame, is no longer used, because we have better ways of getting high temperatures. It is similar in construction, however, to other appliances we do use, and it is of interest from a historical standpoint.

The oxyhydrogen blowpipe was devised by the American chemist Robert Hare (Fig. 76) more than one hundred years ago. It consists of two tubes, one inside the other, as shown in Fig. 77. Hydrogen enters through the tube *H*, is led through the outer tube *B*, and is set on fire at the end of the tube at *A*. Oxygen, entering at *O*, is led through the inner tube *C*. In this way the two gases are brought together at the end of the tubes at *A*, pure oxygen being supplied to the burning hydrogen. The flame is so hot that it will melt platinum, which melts at 1755°, while iron melts at 1535°. As far back as 1860 the famous French chemist Sainte-Claire Deville, using a furnace heated by an oxyhydrogen blowpipe, melted as much as fifty pounds of platinum at one time.

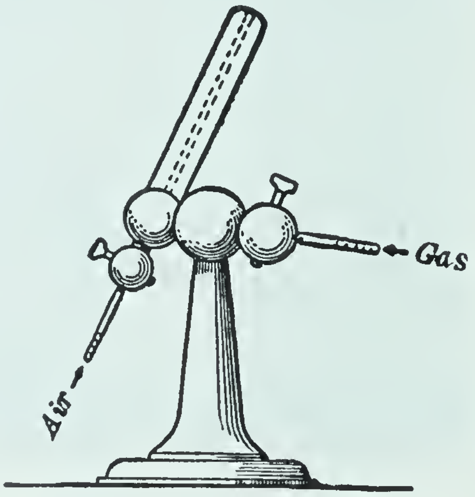


FIG. 78. The ordinary laboratory blast lamp

The blast lamp, a child of the oxyhydrogen blowpipe. The oxyhydrogen blowpipe has given way to a similar form of apparatus (which will be described later) in which the gas *acetylene* is used in place of hydrogen. But every chemical laboratory uses an almost exact copy of the oxyhydrogen blowpipe, called the *blast lamp* (Fig. 78). This child of the old blowpipe conveniently uses gas from the gas tap instead of hydrogen, and compressed air instead of oxygen. Of course it does not give as much heat as the original blowpipe, but it does very well for most laboratory uses.

CHAPTER SUMMARY IN QUESTION FORM

1. Name three important uses of hydrogen.

2. Give the form (free or combined) and relative abundance of hydrogen in each of the following: (*a*) earth's crust; (*b*) water; (*c*) earth's atmosphere; (*d*) sun's atmosphere; (*e*) the human body.

3. Who first obtained hydrogen in a pure state and recognized it as a new gas?

4. (*a*) What name did the discoverer of hydrogen give to the gas? (*b*) Who gave it its present name? (*c*) Is it an appropriate name?

5. Give two general ways for preparing hydrogen from water.

6. Explain what takes place when sodium acts on water.

7. Explain what takes place when steam is passed over hot iron.

8. (*a*) What element is present in all acids? (*b*) How can you often set it free?

9. Explain in detail the usual laboratory method for preparing hydrogen, giving the names of the substances used and the products formed.

10. Mention one very important precaution that should be taken in preparing hydrogen.

11. Compare hydrogen and oxygen as to (*a*) weight; (*b*) color; (*c*) odor; (*d*) taste; (*e*) solubility in water; (*f*) effect on body when breathed.

12. (*a*) With what element does hydrogen have a great affinity? (*b*) What is formed when these two elements combine?

13. (*a*) Is it dangerous to mix hydrogen and oxygen under ordinary conditions? (*b*) Under what conditions does such a mixture become dangerous?

14. In the ordinary meaning of the terms, should you say (*a*) that hydrogen burns or (*b*) that it supports combustion?

15. What properties of hydrogen are shown by pushing a lighted candle into an inverted cylinder of hydrogen?

16. Define the following terms and give an example to illustrate each: (*a*) oxidation; (*b*) reduction; (*c*) oxidizing agent; (*d*) reducing agent.

17. Tell what takes place when hydrogen is passed over hot copper oxide.

18. What substance found in large quantities in nature consists chiefly of compounds of hydrogen united with carbon?

19. (*a*) Draw a diagram of the oxyhydrogen blowpipe and explain the way it works. (*b*) Contrast it with the ordinary laboratory blast lamp.

THOUGHT QUESTIONS

1. Zinc is an element and a solid; yet bubbles of gas rise from its surface when it is placed in dilute sulfuric acid. Explain.

2. What factors determine the choice of a method for preparing a substance (*a*) in the laboratory? (*b*) commercially (that is, on a large scale)?

3. In Fig. 74, why do we dry the hydrogen before passing it over the copper oxide?

4. Which explodes the more violently, (*a*) a mixture of hydrogen and oxygen or (*b*) a mixture of hydrogen and air? (*c*) Explain.

5. Explain what takes place when a lighted candle is introduced into a cylinder (*a*) of hydrogen; (*b*) of air; (*c*) of oxygen; (*d*) of a mixture of hydrogen and air; (*e*) of a mixture of hydrogen and oxygen; (*f*) of a mixture of oxygen and air.

6. (*a*) An ideal gas for inflating balloons should have what properties? (*b*) Does hydrogen have these properties? (*c*) Would oxygen do for this purpose?

7. Hydrogen passed over hot copper oxide forms water and copper. What does this prove about the composition of water?

8. Which gives the hotter flame, (*a*) the oxyhydrogen blowpipe or (*b*) the blast lamp? Give reasons for your answer.

9. An ordinary five-cent piece weighs about 5 g. (*a*) What volume of hydrogen would weigh a like amount? (*b*) What volume of oxygen?

10. 100 g of water contains how many grams of hydrogen?

11. Which of the following statements are true and which false? (*a*) When hydrogen is passed over hot copper oxide, the oxide is reduced. (*b*) Copper oxide is a good reducing agent. (*c*) When hydrogen combines with other elements, water is always formed. (*d*) Air is an oxidizing agent. (*e*) When sodium reacts with water, all the hydrogen of the water is set free. (*f*) Both hydrogen and oxygen were known at the time the Declaration of Independence was signed.

OPTIONAL EXERCISES

1. Devise a simple experiment to prove that hydrogen is lighter than either oxygen or air.

2. As has been stated, water contains about eight times as much oxygen as hydrogen by weight. Yet when we decompose water by the electric current, the oxygen obtained has only half the volume of the hydrogen (Fig. 55). Explain.

3. Suppose you have a quantity of sulfuric acid containing 100 g of hydrogen sulfate. (*a*) What weight of hydrogen is present in it (p. 104)? (*b*) If you liberate this hydrogen, what volume will it occupy?

4. (*a*) Calculate the approximate weight of hydrogen in your body. (*b*) What volume would this have if it were set free?

5. (*a*) How large a bottle, measured in liters, will 1 g of hydrogen fill? (*b*) 1 g of oxygen?

CHAPTER IX

Water

[The Most Important Liquid in the World]

We live in a world of water chemistry. We often hear that we are living in an age of metals, and in an industrial sense this is true. But the chemistry of our lives and of the world we live in is a water chemistry. Aside from petroleum, water is the only liquid found abundantly in nature. It covers about five sevenths of the surface of the earth, in some places to a depth of five or six miles. It constitutes our oceans, lakes, rivers, and springs. As vapor it is one of the more important gases of the atmosphere. As ice it deeply covers both poles of the earth.

Water forms a part of many rocks, and of every plant and animal that grows. If your weight is 150 lb, over 100 lb (70 per cent of your weight) is water. If you buy 100 lb of food, — meat, peas, potatoes, apples, oranges, — you buy at least 75 lb of water. If, instead, you buy celery, tomatoes, lettuce, cabbage, and spinach, your purchase of water is more than 90 lb (see table, p. 491). Even dry-looking things, such as wood, coal, and many minerals, give up water when heated. Some astronomers can find nothing but water over the entire surface of the planet Venus. We cannot imagine any form of life without water; and since our moon has no water, we feel sure it has no life.

Water is a compound. It was long thought to be an element. Then, about a hundred and fifty years ago, there was a great stir among chemists. The Englishman Cavendish (Fig. 68) and the Frenchman Lavoisier (Fig. 58) proved it to be a compound of oxygen and hydrogen. This discovery was almost as exciting then as if someone today were to prove that iron or copper is a compound of two gases.

Properties of water — some very familiar, others not. Pure water has no odor or taste. We think it is colorless; but if we look through a great thickness of it, we can see that it has a bluish tint. It freezes at 0° and boils at 100°.

When water at 100° is cooled, it steadily contracts until

FIG. 79. This fountain in Munich, Germany, was designed to show that water may act either as friend or as foe

it reaches 4°; then, unlike most other liquids, it expands as the temperature falls until it reaches the freezing point. A definite volume of water, then, at 4° is heavier than the same volume at any other temperature; and it is because of this that ice floats in water, while most other solids sink to the bottom of their liquids as they freeze. One ml of water at the temperature of greatest density — namely, 4° — weighs almost exactly 1 g; indeed, for all practical purposes we may forget the inexactness and say that *1 ml of water at 4° weighs 1 g.*

How water acts chemically. Since water contains both oxygen and hydrogen, we might expect it to give up oxygen and so act as an oxidizing agent (p. 110), or give up hydrogen and act as a reducing agent (p. 110). But the oxygen and the hydrogen are too strongly bound together to part company except under unusual conditions. Water is not decomposed by heat to any extent we can ordinarily notice. Even when heated to twenty-five times its boiling point, the steam is only slightly decomposed, and the resulting oxygen and hydrogen combine again completely at a lower temperature. A compound, such as water, that resists decomposition by heat is called a *stable* compound. In other ways water can be decomposed. The electric current will do it (Fig. 55), and so, too, will some of the metals (p. 104).

Water helps along many reactions — is a catalyst. A great many reactions will not go on at all if the substances concerned are *perfectly dry*, but even a *trace* of water will start them going. For example, we have seen that phosphorus burns vigorously in oxygen (p. 91). If, however, both the phosphorus and the oxygen are *completely* dry, they will not combine at all. Why this should be so we do not know. Nevertheless, we do know that water serves as a very good catalyst for many reactions.

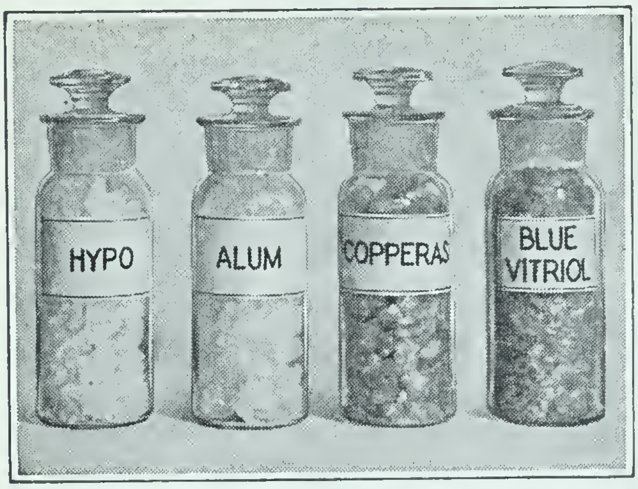


Fig. 80. Some common hydrates

Water will combine with some compounds — hydrates. Water combines directly with many compounds, and the resulting solids (usually crystalline) are perfectly dry. Such compounds are called *hydrates*. Many well-known compounds, such as alum and blue vitriol (Fig. 80), belong to this class. When a hydrate is heated, the water can all be driven off again; and the compound left is said to be *anhydrous*, which means "without water." The combined water in a hydrate is called *water of hydration*. Sometimes it is called *water of crystallization*; but this term is misleading, since many crystals, like those of common salt, are anhydrous, while some hydrates are not crystalline.

Efflorescent compounds. This means "powder-forming" compounds. It often happens that the water of a hydrate is not held very firmly by the compound, which means that the affinity between the two is not very strong. When such crystals are exposed to dry air, the water is slowly given off as water vapor, and the crystal then crumbles to a powder. Such a compound is said to be *efflorescent* (Fig 81).

Natural waters are never pure. We have already learned that pure water is a compound containing 11.19 per cent of hydrogen and 88.81 per cent of oxygen by weight. It is a well-known fact that water readily dissolves such substances as salt and sugar. It also dissolves certain gases present in the air, as well as many of the constituents of all soils. It is evident, then, that natural waters will never be entirely pure but will contain in solution various gases and mineral matter dissolved from the air, the soil, and the rocks with which these waters come in contact. One liter of ocean water contains about 40 g of mineral matter, over three fourths of which is common salt. River waters and well waters contain much less — most of them not more than 1 g to the liter.

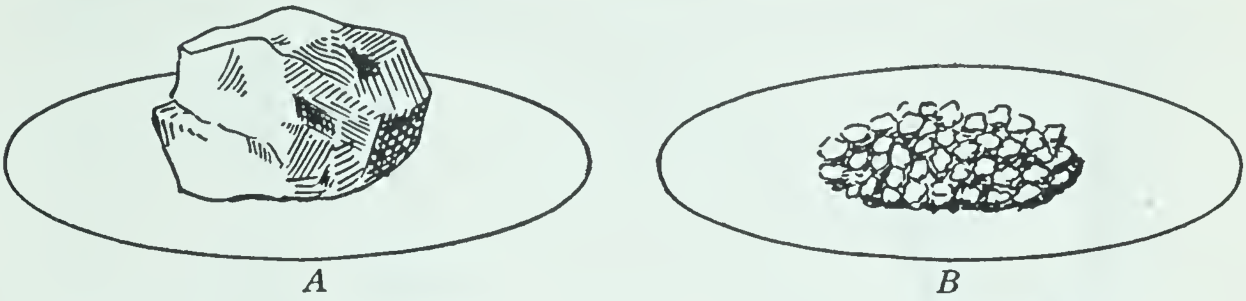


FIG. 81. A crystal of the efflorescent compound *A*, on exposure to dry air, slowly crumbles, as shown in *B*

Most natural waters contain bacteria. In addition to gases and mineral matter, most natural waters contain microscopic living organisms called *bacteria* (Fig. 82). This is especially true of waters in densely populated districts, where sewage refuse is likely to find its way into streams. For such refuse not only contains these organisms but serves as food for them, and they rapidly multiply in its presence.

Effect of foreign matter in water on health. The mineral matter in water rarely has any injurious effect on health. Indeed, it may supply material for building up the solid tissues of the body, and water with an ordinary mineral content is to be preferred to absolutely pure water. Many of the bacteria are also without injurious effect, and may even purify the

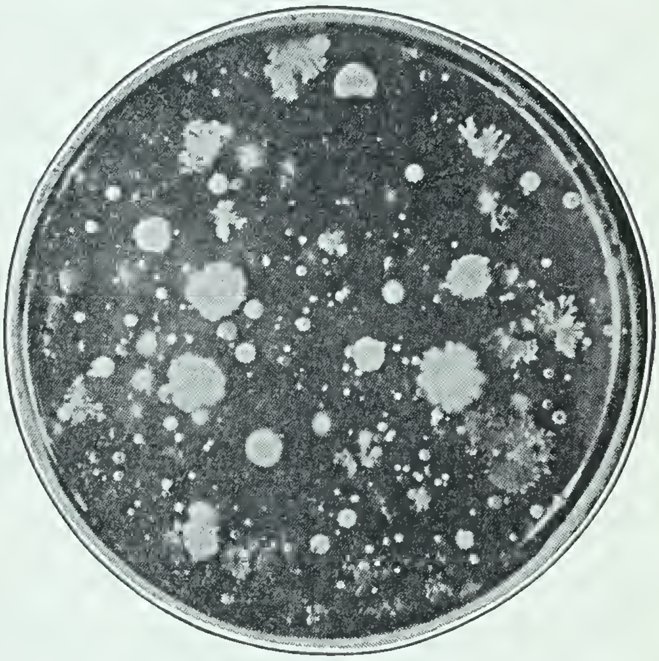


FIG. 82. Bacteria in impure water

Colonies of bacteria growing in gelatin to which a few drops of water have been added. Each colony corresponds to a single bacterium in the original water

water by destroying the food upon which bacteria live. Others, however, are the direct cause of certain diseases.

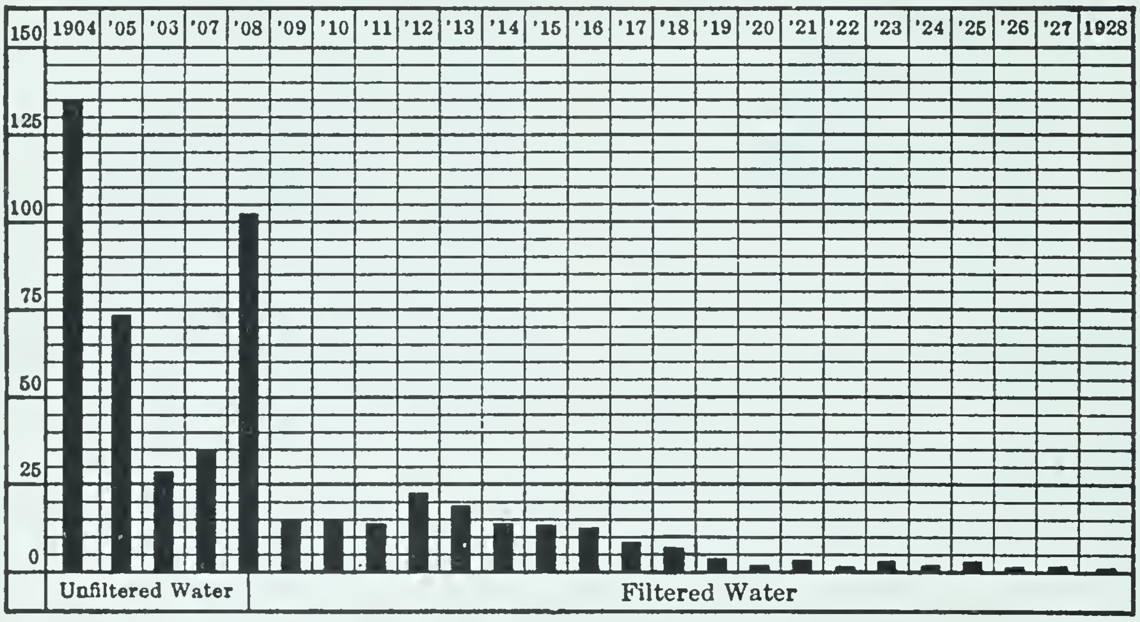


Fig. 83. Chart giving the typhoid-fever death rate, over a number of years, per 100,000 of population in Columbus, Ohio

The chart shows the effect of water purification in decreasing the ravages of this disease. Since 1928 the death rate has nearly vanished

For example, typhoid fever is due to a certain bacterium that gets into the human body chiefly through the drinking water; and this much-dreaded disease has been largely stamped out by purifying our water supplies (Fig. 83). The appearance of a water is no assurance of its purity. Only the trained chemist and bacteriologist can make tests that are trustworthy.

How can natural waters be purified? Pure water is necessary for many purposes. It would not do, for example, to fill up our automobile batteries with natural water (save in a few favored places); for the mineral matter in the water would injure them. The chemist has especial need of pure water. To get it he boils the natural water and cools, or *condenses*, the steam in clean vessels. The process is called *distillation*, and the purified water so obtained (the *distillate*) is called *distilled water*. The mineral matter is all removed; for it is not volatile and remains in the vessel in which the water is boiled. The process of distillation is usually carried out as shown in Figs. 84 and 85.

Ordinary "pure water." Ordinarily, when we speak of "pure water," we do not mean water from which *all* foreign matter has been removed, but simply water that contains nothing injurious to health. Since it is the bacteria present that make water dangerous, it is necessary only to destroy these to get wholesome water. This can be done by distillation, and distilled water is often sold for drinking purposes. The same end can be gained by simply boiling the water for

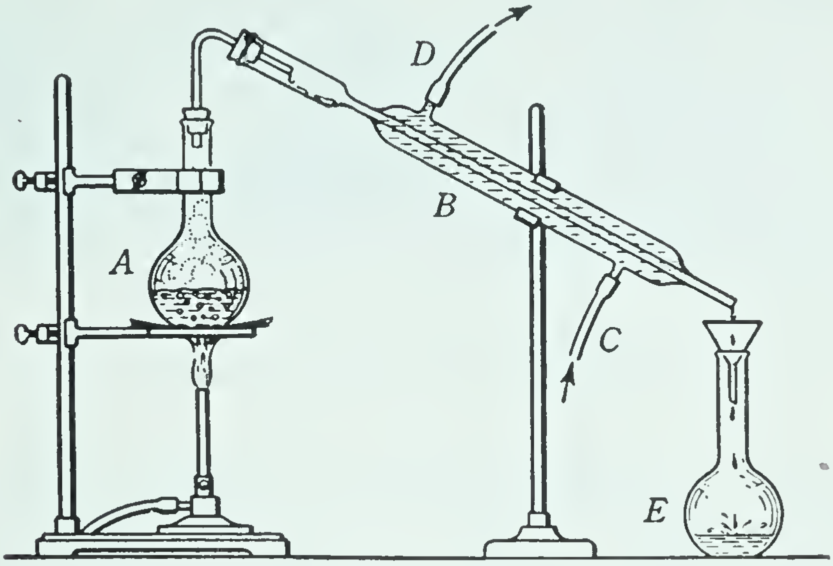


Fig. 84. Laboratory distillation

Natural water is boiled in the flask *A*, and the resulting steam is led through the inner tube of the condenser *B*, which is kept cold by tap water entering at *C* and flowing out at *D*. The steam condenses in the cold inner tube and the resulting water collects in the flask *E*. Why is the cold water made to enter the condenser at *C* rather than at *D*?

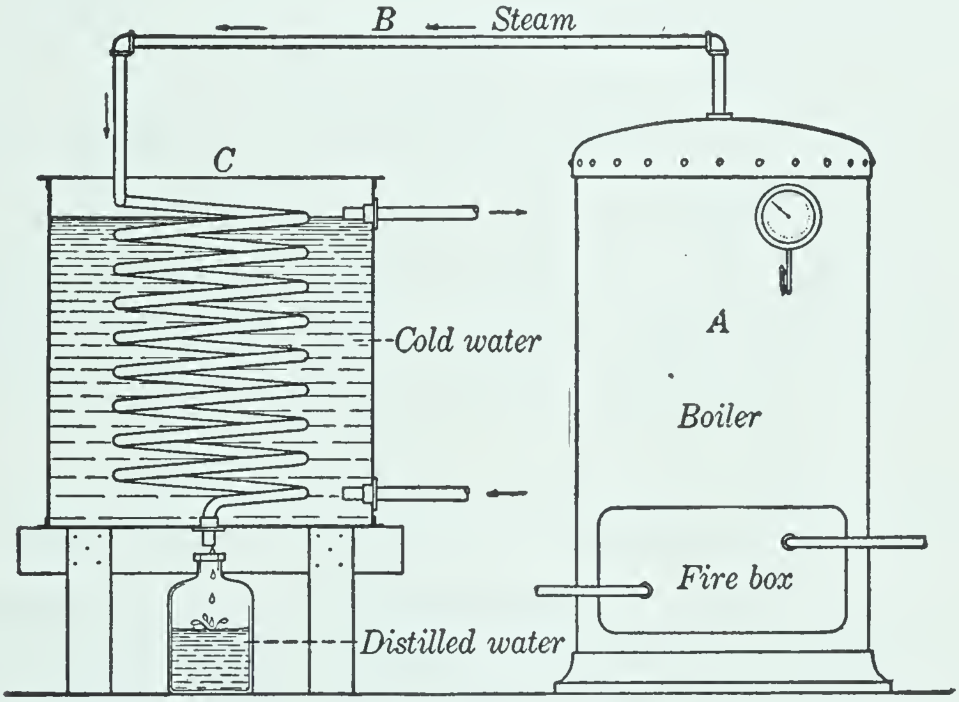


Fig. 85. Distillation on a large scale

In commercial distillation the natural water is boiled in the large boiler *A*, and the steam is conducted through *B* into the condenser *C*, consisting of a coiled metal tube (usually made of tin) surrounded by cold water

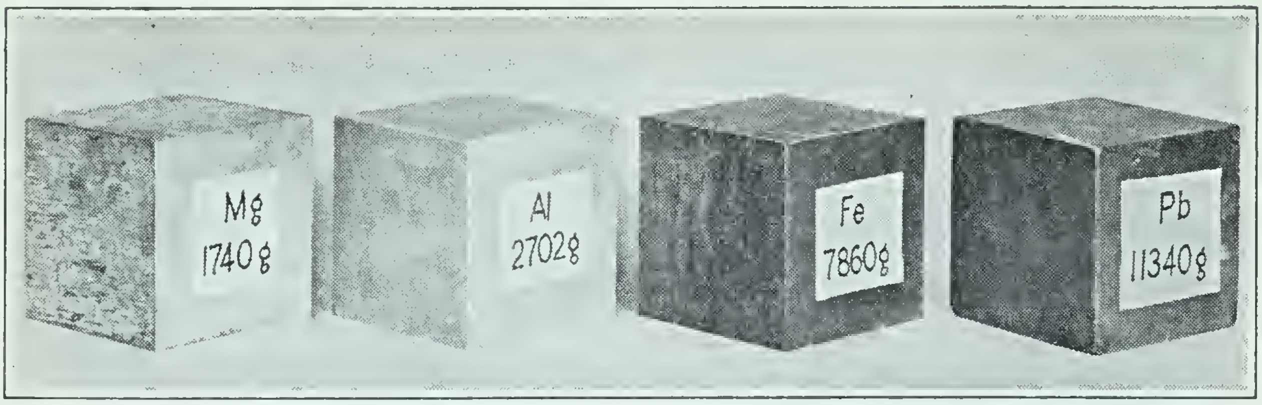


Fig. 86. The figure gives the weight of 1000 ml of each of the four metals shown. What is the density of each of the metals?

a few minutes; for the heat kills the bacteria. But, plainly, these methods cannot be used for purifying the water supply of a large city. The methods used for such purposes will be explained in a later chapter (Chap. XLVII) after the chemical processes employed have been studied.

Water is used as a standard unit. Water has a number of properties that have led chemists to use it as a standard for various measurements. It is a liquid, so that both its weight and its volume can be measured precisely. It is easily purified; hence its true freezing and boiling points can be measured accurately, and both points are convenient temperatures.

So in science the freezing point of water is marked 0° and its boiling point 100° on the centigrade scale for measuring temperatures (see Appendix B). The unit of weight, the gram, was defined as the weight of 1 ml of water at its temperature of greatest density, namely 4°. The unit of heat, the calorie, is the quantity of heat required to raise the temperature of 1 g of water one degree (p. 56). These are a few of the units based on water that the chemist often uses.

What is meant by the term *density*? We hear it said that some substance is denser than some other substance; for example, that gold is denser than water. Just what do we mean by this statement? By the density of a substance we mean the mass (quantity of matter) in a unit volume.

Although there is a distinction between the terms *mass* and *weight*, for our purposes we may use these terms interchangeably. Then, adopting the gram as the unit of weight, and the milliliter as the unit of volume, we may define density as follows:

The density of any substance is the weight in grams of 1 ml of the substance (Fig. 86).

What is meant by *specific gravity*? On the labels of bottles of various liquids, such as oils or acids, we often see the words *specific gravity* (or *sp. gr.*) instead of *density. Specific gravity* is a purely relative term. The specific gravity of a liquid is the *ratio* by weight between the weight of any given volume of the liquid and that of an equal volume of some other liquid chosen for comparison. Any convenient units of weight and volume may be used. We may choose a cubic foot or a cubic inch as the volume, and pounds or ounces as units of weight. In chemical industries the usual standard chosen is water, at room temperature (18° or 20°), measured in milliliters and grams. If water at 4° is chosen, then the density and the specific gravity have the same number value. For at that temperature the unit volume of water (1 ml) weighs 1 g.

The density of gases. Gases are so light that it is not convenient to define their densities as the weight of 1 ml. We sometimes compare them with air as the unit standard. More often we give the weight of 1 *liter* of the gas in grams. This number is sometimes called the *liter-density* of the gas. On the page facing the back cover is given the weight of 1 liter of each of the common gases, and in Appendix E are given the densities of a number of the elements.

CHAPTER SUMMARY IN QUESTION FORM

1. Where is water found in nature?

2. (*a*) Mention some foods that have a very high water content; (*b*) some that have less water.

3. What is the approximate weight of water in your body?

4. Who first proved water to be a compound?

5. (*a*) Show how the volume of a definite weight of water varies with its temperature. (*b*) What is the temperature of water at its maximum density?

6. Should you say that 1 ml of water weighs 1 g at 0°, at 100°, at 4°, at 75°, or at all temperatures?

7. We say that water is a *stable* compound. Explain what is meant by this statement.

8. Give two ways of easily decomposing water.

9. Water is a good *catalyst.* Explain, and give examples to illustrate.

10. (*a*) Distinguish between the terms *hydrates* and *anhydrous.* (*b*) Give examples to illustrate.

11. What is an *efflorescent* compound?

12. Knowing the properties of water, should we expect chemically pure water to be found in nature?

13. (*a*) What kinds of impurities are found in natural waters? (*b*) What is the effect of each on our health when natural waters are used for drinking?

14. (*a*) How can we remove all impurities from natural waters? (*b*) Draw a diagram of the apparatus used and explain the process.

15. (*a*) Is it necessary to remove all impurities from water in order to make it safe for drinking? (*b*) What other method could we use?

16. Water is taken as a standard in what measurements?

17. What word is used to designate the weight of a unit volume of a substance?

THOUGHT QUESTIONS

1. Can you tell how pure a given water is by its appearance?

2. Compare the meaning of the term *pure water* as used by the chemist with its meaning as used in our homes.

3. How could you tell whether a given sample of water is distilled water?

4. How could you measure the total amount of solid matter in any given sample of water?

5. The taste of water is changed by distilling the water, but can be restored in part by stirring or shaking it. Explain.

6. Compare the properties of water with the properties of the elements that compose it.

7. (*a*) What is the average amount of water in pure milk? (See table, p. 491.) (*b*) How could you tell whether the milk sold you was *watered*?

8. Why do the chemist and the pharmacist use distilled water rather than water that has simply been boiled?

9. Why do the water pipes in our homes burst when the water in them freezes?

10. Water is eight-ninths oxygen. Why is it not a good oxidizing agent?

11. Referring to the table in Appendix E, give the weight of 1 ml of each of the following elements: (*a*) sodium; (*b*) magnesium; (*c*) gold; (*d*) platinum; (*e*) tin.

12. Assuming the densities of alcohol, water, and sulfuric acid to be 0.8, 1, and 1.84, respectively, calculate the weight of each of these liquids required to fill a bottle holding 25 ml.

13. Suppose you had a cube of iron that had a volume of 1000 ml. How large a cube of gold would be required exactly to balance it on the scales?

OPTIONAL EXERCISES

1. Water collects on the outside of a glass filled with ice water. It collects on the inside of a cold glass inverted over a burning candle. Explain the source of the water in each case.

2. Make a drawing of the apparatus used in your laboratory for obtaining distilled water.

3. Prepare an exhibit of four or five different kinds of food, say, an apple, a potato, a tomato, lettuce, flour. Place by the side of each a tube containing the amount of water present in it. (For the percentage of water present in each food see table, p. 491.)

CHAPTER X

The Composition of Water; Hydrogen Peroxide

[Two Compounds Composed of the Same Elements]

I. THE COMPOSITION OF WATER, A GREAT PROBLEM FOR THE CHEMIST

How can we be sure of the composition of water? On page 26 it was stated that water contains 88.81 per cent of oxygen by weight and 11.19 per cent of hydrogen. How do chemists know this? How can they find out the composition of *any* compound? The answer is, By experiment. Now there is no general way, no rule of thumb, by which these experiments are to be made. Each compound makes a new problem, and the chemist must find ways and means to fit each particular case.

But he always follows what may be described as one or the other of two different *plans of work.* Let us look at these two plans before we take up the particular problem of the composition of water.

The method of analysis — Plan 1. *Analysis* means "taking apart." By the analysis of a compound we mean taking it apart into the elements that compose it and weighing each one separately. For example, let us suppose we have found some means of decomposing water. Let us further suppose that suitable tests have shown that the elements in water are oxygen and hydrogen only.

Now we must begin to use the balance. We first weigh out some definite quantity of water — say, 100 g. Then we decompose this water, collect the oxygen and hydrogen separately, and weigh each. We now know the weight of the water we started with and the weight of each element that is in it. We can at once express the weight of the oxygen and the hydrogen as fractions or percentages of the weight of water. We have made an analysis of water. This is a *general plan* of work. The actual experiments are never quite as simple as this description might lead us to expect.

The method of synthesis — Plan 2. *Synthesis* means "putting together." It is just the opposite of analysis. In using the method of synthesis for getting at the composition of a compound we must first find what elements are present in the compound, then the proportion in which the elements combine, and finally the weight of the compound formed by the union of definite weights of each of the elements. The plan seems simple, but it usually requires a good deal of ingenuity to carry it out. In the case of water it turns out that the method of synthesis is the easier to follow, and we shall now study some details of the method. The synthesis and analysis of water are important in themselves, but it is even more important to be thinking of general plans of work.

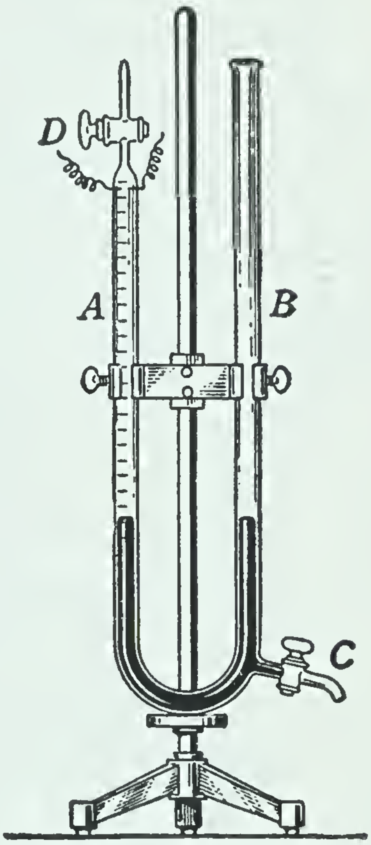


FIG. 87. A convenient form of eudiometer

It is used to determine the composition of water

Synthesis of water by volume. In this experiment we must take the following steps: (1) Measure out definite volumes of both oxygen and hydrogen. (2) Cause the two gases to combine, and measure the volume of the gas left over. (3) Calculate the results.

1. ***The measurement of the two gases.*** The vessel used to measure the gases is called a *eudiometer* (Fig. 87). It is a glass tube bent in the shape of the letter U. It is open at one end, and closed at the other by a stopcock. Near the closed end two wires are sealed through the glass, with their ends nearly meeting inside the tube. These wires enable us to pass an electric spark through the gases in the tube so as to start their union. The spark plug and explosive mixture in the cylinder of an automobile engine work in the same way.

The eudiometer is first filled with mercury (Fig. 87), in which neither of the gases is soluble. A small volume of hydrogen (say, 20 ml) is then admitted to the branch *A* of the eudiometer through the stopcock *D*. The stopcock is then closed, and mercury is drawn off through the stopcock *C* until the level of the mercury is the same in each branch of the eudiometer, as shown in the figure. The enclosed hydrogen is now under atmospheric pressure, and its volume is accurately read off on the scale of the eudiometer.

About an equal volume of oxygen is next admitted to the eudiometer in just the same way. The mercury in the two branches is brought level, and the total volume is carefully read. The volume of the oxygen is found by subtracting the volume of the hydrogen from that of the total volume. We now have measured volumes of both hydrogen and oxygen enclosed in the same tube.

2. ***The combination of the two gases.*** A small induction coil, operated by an electric battery, is now connected with the wires sealed in the eudiometer, and a spark is passed through the mixed gases. At once there is a small explosion within the tube. The mercury in the branch *A* is at first pushed down by the force and heat of the explosion, but immediately rises again to take the place of the gases that have combined to form water.

Mercury is now added to the branch *B* of the eudiometer until its level in the two branches is the same, and the volume of the left-over gas is read off. (We may disregard the volume of the water formed, because it is too small to be measured.) This gas must next be tested to see whether it is oxygen or hydrogen; for experiment has shown that one of the two is always completely used up. If we used about equal volumes of hydrogen and oxygen, experiments show that the gas left in the tube is pure oxygen.

3. ***The calculation.*** From the foregoing measurements we can at once calculate the composition of water. Let us suppose the measured volumes were these:

1. Volume of hydrogen introduced into the tube	20.2 ml
2. Volume of hydrogen and oxygen introduced	40.2 ml
3. Volume of oxygen (difference between volumes 1 and 2)	20.0 ml
4. Volume of gas (proved to be oxygen) left after explosion	9.9 ml
5. Volume of oxygen that combined with hydrogen (difference between volumes 3 and 4)	10.1 ml

Since the gas left over at the end of the experiment was all oxygen, we know that all the hydrogen, 20.2 ml, has been used up to form water. So 20.2 ml of hydrogen has combined with 10.1 ml of oxygen to form water. In general terms, *2 volumes of hydrogen combine with 1 volume of oxygen to form water.* Since 1 liter of hydrogen weighs 0.08987 g, and since 1 liter of oxygen weighs 1.429 g (table on inside back-cover page), it follows that the proportion *by weight* in which the two gases unite is 2 × 0.08987 : 1.429, or 1 : 7.94; that is, 88.81 per cent oxygen and 11.19 per cent hydrogen.

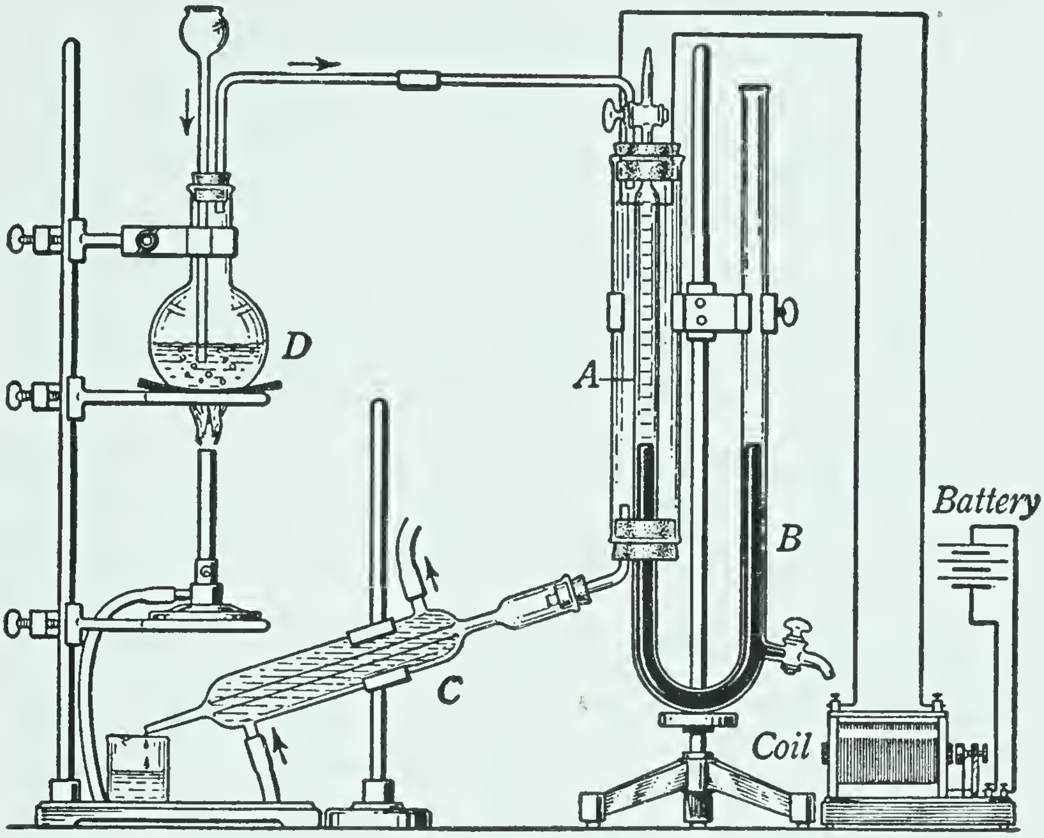


FIG. 88. Apparatus for determining the ratio by volume in which oxygen and hydrogen combine, and the ratio of each of these volumes to the volume of the steam formed

The water formed by the union of measured volumes of oxygen and hydrogen in the eudiometer *B* is kept in the state of gas (steam) by heating a high-boiling liquid in *D* and conducting its hot vapor into the jacket tube *A* surrounding the one branch of *B*. The vapor is then condensed in the condenser *C*

All these measurements must be carried out at the same temperature and pressure. Since all gases expand and contract equally with changes in temperature and pressure, it does not make any difference what the temperature and pressure are, so long as one gas is not measured at one temperature and pressure and the other at a different one. You see that Charles's law saves us some trouble here.

Some other striking volume relations. It is certainly most unexpected to find that hydrogen and oxygen unite *by volume* in the exact ratio of the integers 2 : 1. Since the product of their union (water) is easily changed into a gas (steam), we wonder how the volume of the steam will compare with that of the hydrogen or the oxygen.

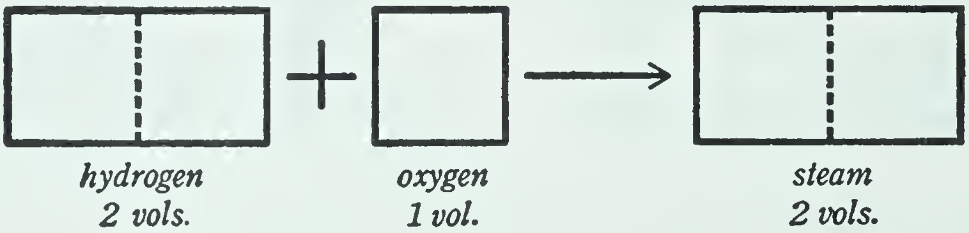
To answer this question we will arrange our eudiometer as shown in Fig. 88. The branch *A* of the tube is surrounded, as shown in the figure, by steam (or by the vapor of some liquid with a boiling point higher than that of water (100°)). The combination of the oxygen and hydrogen is brought about at this higher temperature, the water formed remaining as steam. The results of this experiment are most interesting, as shown in the following equation:

20.2 ml hydrogen + 10.1 ml oxygen → 20.2 ml steam

or

2 vols. hydrogen + 1 vol. oxygen → 2 vols. steam.

We can picture these relations graphically as follows:



The experiments just described prove the following:

There is a simple ratio (of integer numbers) between the volumes of hydrogen and oxygen that combine, and between the volume of either one of them and that of the steam formed by their union.

No one would have imagined that this is so before experiment brought the facts to light.

Synthesis of water by weight. On page 108 we found that hydrogen, when passed over hot copper oxide, takes away oxygen from the oxide (reduces it) and forms water. Starting from these facts we can devise a way to find out the composition of water *by weight.* Copper oxide is placed in the tube *A* (Fig. 89), and the tube and its contents are then carefully weighed. The tube *B* contains calcium chloride, which, it will be remembered, readily combines with water vapor. Tube *B* and its contents are also carefully weighed.

The oxide is now heated, as shown in Fig. 89, and a current of *pure, dry* hydrogen is passed into the tube *A* at *C.* The hydrogen combines with the oxygen of the copper oxide, forming water (as vapor). This is swept along by the excess of hydrogen and is absorbed by the calcium chloride in tube *B*. When the copper oxide has been reduced, the heating is stopped, and the tubes *A* and *B* are allowed to cool to room temperature.

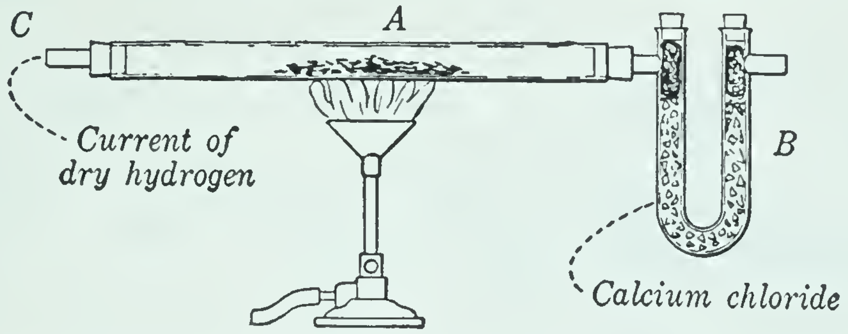


Fig. 89. Apparatus for finding the ratio by weight in which oxygen and hydrogen combine to form water

The tube *A* and its contents are again weighed. The loss in weight is the weight of the oxygen taken from the copper oxide to form water. The tube *B* and contents are also weighed. The increase in weight gives the weight of the water formed. The weight of the hydrogen used up we can get indirectly — by subtracting the weight of the oxygen from that of the water formed. From the results of an actual experiment we can make the necessary simple calculation, as follows:

1. Loss of weight of tube *A* and contents (oxygen used)	2.4 g
2. Gain in weight of tube *B* and contents (water formed)	2.7 g
3. Weight of hydrogen in the water formed (weight 2 − weight 1)	0.3 g

So 0.3 g of hydrogen combines with 2.4 g of oxygen to form 2.7 g of water. In round numbers, 1 part by weight of hydrogen combines with 8 parts by weight of oxygen.

Results do not entirely agree. What then? It turns out that no one can repeat his own experiment and get absolutely the same result the second time. No two men will get exactly the same figures. Two different methods are likely to lead to values that are still farther apart. Of course, if the work is carefully done and the method is a good one, the results obtained will all be close together, but not quite the same. What shall we do?

Well, we just use common sense. If all the experiments seem to be done with equal care and the methods are equally reliable, we simply average all the results to get the most probable figures. If some one man's work stands out as having been done with remarkable skill and his plan of work seems better than any other plan, we adopt his results and let all others go. This is what a jury has to do at a court trial. No two witnesses of an occurrence can ever tell quite the same story, no matter how honest they may be. The jury has to come to its decision by carefully weighing all the evidence put before it.

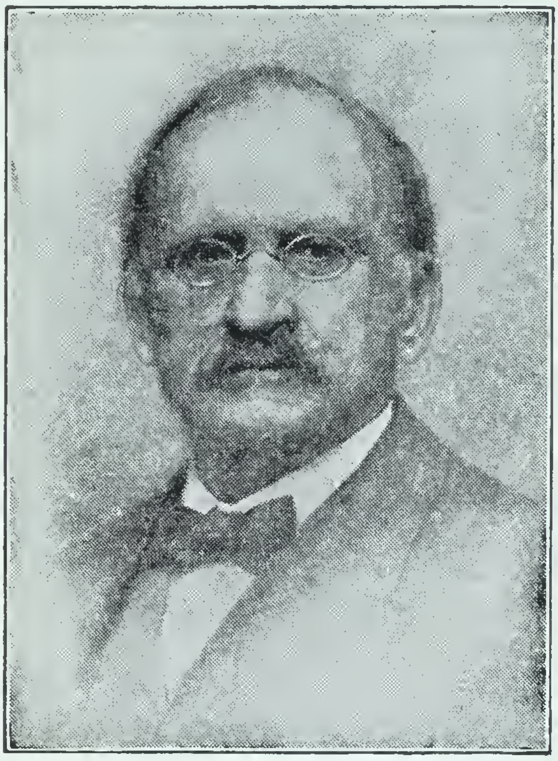


Fig. 90. Edward Williams Morley (1838-1923)

Former Professor of Chemistry in Western Reserve University. Known for his accurate measurements of the densities of oxygen and hydrogen and of the ratio in which they combine to form water

All chemists agree that the results obtained for water by the American chemist Morley (Fig. 90) are the most accurate. Not only was Morley a most skillful experimenter, but he spent many years on the problem of measuring the exact composition of water. His results are as follows:

Water is a compound containing oxygen and hydrogen in the ratio of 1 part by weight of hydrogen to 7.94 parts of oxygen; or, expressed in percentages, 11.19 per cent of hydrogen and 88.81 per cent of oxygen

The law of definite composition (or of definite proportions). By experiments like the ones just described, chemists have proved that not only water but every pure compound has a perfectly definite composition (Fig. 91). So sure are they of this general fact that when they find that a given substance is constant in its composition they feel pretty certain that it is a definite compound and not a mixture. A generalized statement of these facts is called the *law of definite composition.*

The law of definite composition: The composition of a given chemical compound is always precisely the same.

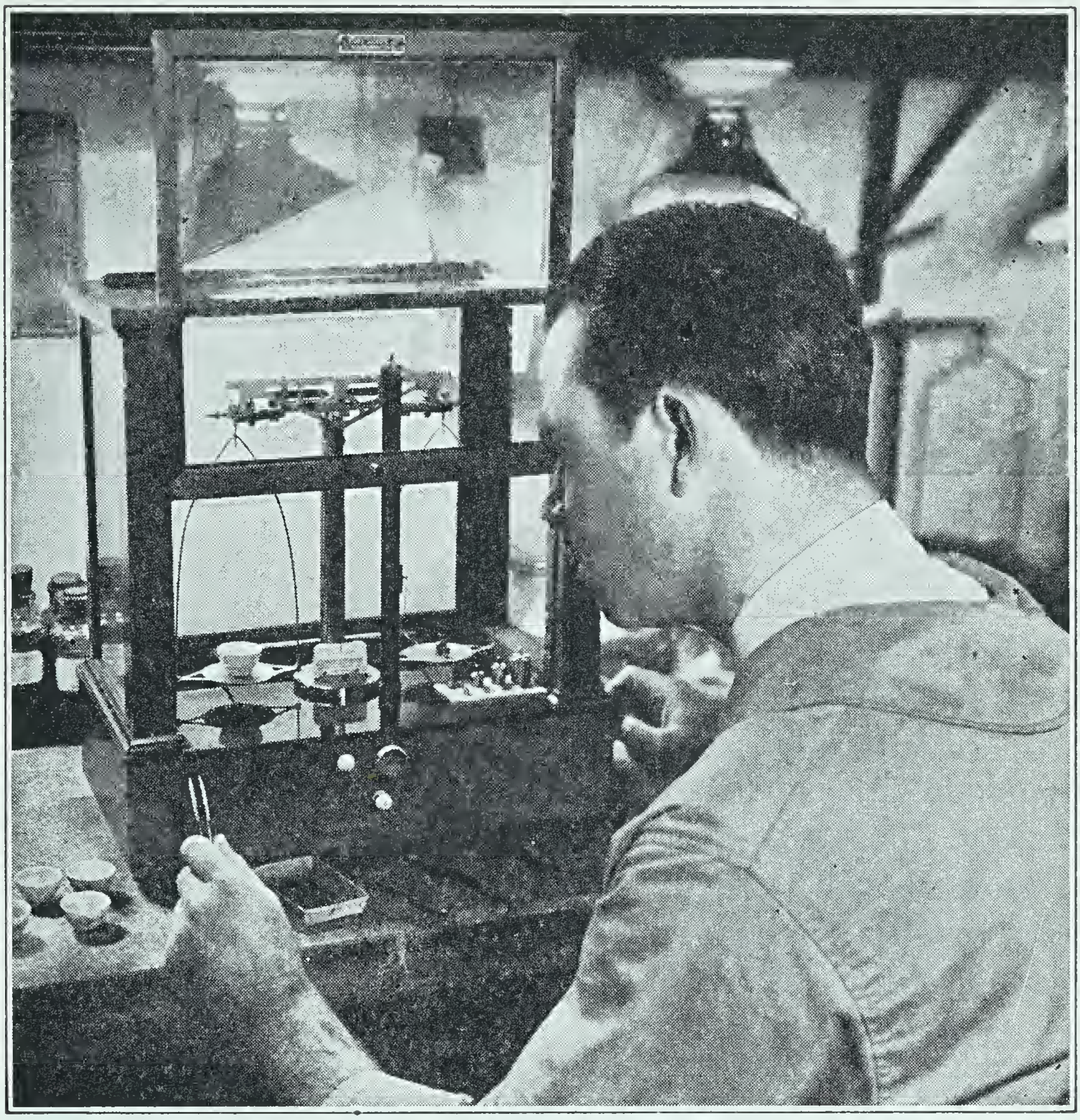


Fig. 91. A chemist determining the composition of a compound

Every chemical laboratory where very accurate work is carried on must have delicate balances weighing to small fractions of a milligram

II. HYDROGEN PEROXIDE, AN UNEXPECTED COMPOUND

Another surprise. The history of chemistry has been full of surprises. Cavendish and Lavoisier surprised the scientists of their time by proving water to be a compound of hydrogen and oxygen. Some forty years later the Frenchman Thénard announced another surprise. He showed that there is a second compound of these two elements which he named *hydrogen peroxide*, and that it has properties very different from those of water. At that time there were other examples known of this same kind — two elements that formed two different compounds by their union; — but no one expected that hydrogen and oxygen belonged to this class. We now know that *most* pairs of elements form two or more distinct compounds.

Water and hydrogen peroxide differ in their composition. Water and hydrogen peroxide are both composed of hydrogen and oxygen only. How, then, do they differ? Experiments show that the difference lies in the proportions in which the two elements are present in the two compounds.

Water contains 1 part of hydrogen by weight to 7.94 parts of oxygen. Hydrogen peroxide contains 1 part of hydrogen by weight to 15.88 parts of oxygen. Water is a very stable compound, and in it every gram of hydrogen holds 7.94 g of oxygen very firmly. Under very special conditions the hydrogen can be induced to take up an extra load of oxygen. But when it does so, each gram has to take up exactly a double load, — no more and no less, — namely, 2 × 7.94 g, or 15.88 g. This is certainly a strange thing.

How we get hydrogen peroxide. Water will not combine with oxygen directly to form this compound with its extra load of oxygen. So we have to make it in a roundabout way. There is an oxide of the metal barium (Ba) called barium peroxide, whose formula is BaO_2. In this compound the barium has an extra load of oxygen. When barium peroxide (hydrated) is put into water and sulfuric acid is added, a reaction takes place which shifts this extra load to the hydrogen of the acid, as shown in the equation

$$\underset{\substack{\text{sulfuric}\\\text{acid}}}{H_2SO_4} + \underset{\substack{\text{barium}\\\text{peroxide}}}{BaO_2} \longrightarrow \underset{\substack{\text{barium}\\\text{sulfate}}}{BaSO_4}\downarrow + \underset{\substack{\text{hydrogen}\\\text{peroxide}}}{H_2O_2}$$

The vertical arrow following the formula $BaSO_4$ means that this compound is a solid that *precipitates* from the solution. A *precipitate* is a solid substance, insoluble in water, that is formed in a reaction. It is separated from the liquid by filtration.

If we study this equation, we shall see that the hydrogen of the acid and the barium of the barium peroxide have simply changed places, and that the two atoms of hydrogen possess twice as much oxygen as they do in water.

The observant student will wonder why we write the formula for hydrogen peroxide H_2O_2 instead of HO. The reason for this is that the formula of a compound represents a molecule, and the molecule of hydrogen peroxide contains two atoms of hydrogen and two atoms of oxygen. Later on we shall see how this fact is known.

What kind of compound is hydrogen peroxide? It is very hard to get this compound in pure form because it goes to pieces so easily, giving up the extra oxygen as gas and forming stable water. When pure it is a colorless, sirupy liquid, much heavier than water (density, 1.44). Dilute solutions in water are much more stable than the pure compound, and druggists sell a solution that contains about 3 per cent by weight of the peroxide.

Uses of hydrogen peroxide. Since hydrogen peroxide gives up oxygen so easily, it is a very good oxidizing agent. All its uses depend on this fact. The cork stopper of a bottle of the peroxide is usually bleached, and this suggests one use. Its main use is as an antiseptic in injuries of various kinds. Apparently its value for this purpose has been rather overrated.

Catalysts are of two kinds — positive and negative. We have described a catalyst as a substance that by its mere presence changes the speed of a reaction (p. 84). In the preparation of oxygen from potassium chlorate, manganese dioxide was found to act as a catalyst to *hasten* the reaction, like oil in machinery; and most catalysts act in this way. We call these *positive* catalysts (Fig. 92).

In the case of hydrogen peroxide we have a compound that decomposes *too easily*. It would be a fine thing if we could find a catalyst that would *slow up* a reaction of this kind. Now just such catalysts are known and are called *negative* catalysts. A substance called acetanilid acts as a negative catalyst in the decomposition of hydrogen peroxide, and a small percentage of this compound is generally present in the peroxide sold by the druggist. Just as we may liken a positive catalyst to oil that will enable us to speed up our automobile, so we may liken a negative catalyst to the brake which we use to slow down the speed.

Another law — the law of multiple proportion. We have seen that one of the most striking facts about the two compounds which hydrogen forms with oxygen is this: for a fixed weight of hydrogen (1 g), hydrogen peroxide has exactly twice as much oxygen as water has.

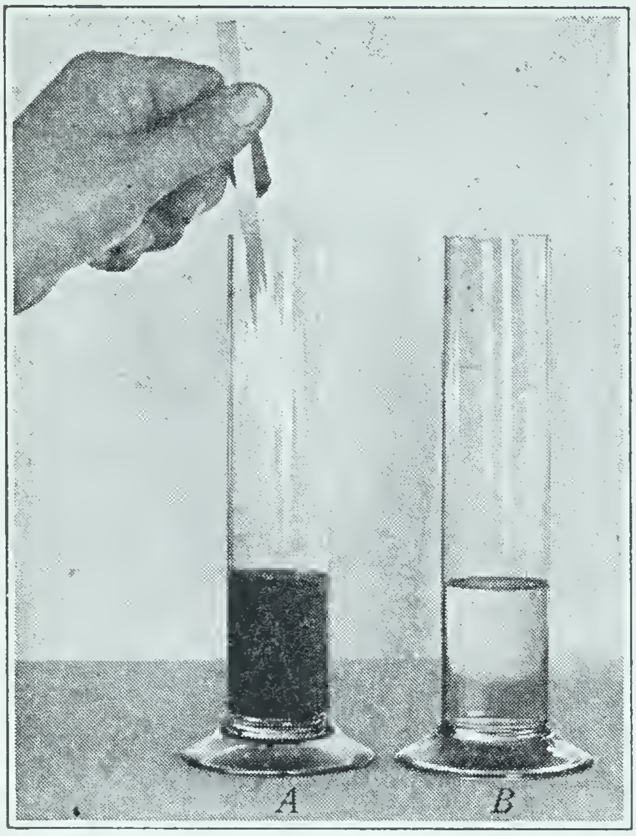


FIG. 92. This figure shows the action of a positive catalyst in decomposing hydrogen peroxide into water and oxygen

The pure peroxide in cylinder *B* decomposes slowly, while that in cylinder *A*, to which some manganese dioxide has been added, quickly decomposes, evolving oxygen as shown in the figure

Now there are a great many pairs of elements that, like hydrogen and oxygen, unite with each other in two or more proportions. In all these cases is it true that for a fixed weight of the one element the weights of the other element are in the ratio of small whole numbers (integers) to each other, such as 1 : 2 or 1 : 3? Thousands of experiments have been made to settle this question, and the answer is, It is always true. This is one of the most important facts in the whole science of chemistry.

This great truth was first recognized by the English scientist John Dalton (Fig. 117) in 1808, and was stated by him in what is called the *law of multiple proportion.*

Law of multiple proportion: When any two elements, A and B, combine to form more than one compound, the weights of A that combine with 1 g of B are in the ratio of small whole numbers to each other.

It should be carefully noticed that this law does not explain *why* this is so, but merely states the facts. That is all any scientific law does.

CHAPTER SUMMARY IN QUESTION FORM

1. Is the composition of a compound determined (*a*) by experiment, or (*b*) by calculation, or (*c*) by both these processes?

2. (*a*) Name the two general classes of methods used in finding the composition of a compound. (*b*) How do these differ from each other?

3. Which of the two methods named in question 2 is better for determining the composition of water?

4. Describe somewhat in detail one method for finding the composition of water, and state the results obtained by this method.

5. Many different chemists have measured the composition of water. Their results do not agree exactly. Explain why this is so.

6. (*a*) Give the name of the chemist who is generally regarded as having measured the composition of water with the greatest exactness. (*b*) State his results.

7. (*a*) In what proportion by volume do hydrogen and oxygen combine to form water? (*b*) Suppose that the two gases are mixed in this proportion, then heated to 100° and exploded; how does the volume of steam formed compare with the volumes of the gases that combined to form the steam?

8. (*a*) Name two compounds that are composed of oxygen and hydrogen only. (*b*) How do you account for the fact that we have two entirely different compounds, yet both are composed of the same elements?

9. Contrast the properties of the two compounds referred to in question 8.

10. What do we call (*a*) a substance that by its mere presence *increases* the speed of a reaction? (*b*) one that similarly *decreases* the speed of a reaction? (*c*) Give a practical example of the use of each of these two kinds of substances.

11. State two laws of chemical combination illustrated by the compounds water and hydrogen peroxide.

THOUGHT QUESTIONS

1. Is ordinary river water (*a*) an element, (*b*) a compound, (*c*) a mixture, (*d*) a suspension, or (*e*) a solution?

2. In measuring the composition of water by volume, why must we take into consideration the temperature and pressure of the hydrogen and oxygen?

3. In the experiment using the apparatus described in Fig. 88, (*a*) why is it necessary to heat the oxygen and hydrogen before combining them? (*b*) To what temperature must they be heated — 90°, 100°, 110°, or 125°?

4. A mixture containing 20 ml of hydrogen and 10 ml of oxygen introduced into a tube at ordinary temperatures and exploded would break the tube into pieces. (*a*) Explain. (*b*) Would the explosion be so violent if you had a mixture of, say, 20 ml of hydrogen and 30 ml of oxygen?

5. Name the gas that would be left, and state the volume it would occupy, after exploding each of the following mixtures: (*a*) 10 ml of hydrogen and 15 ml of oxygen; (*b*) 10 ml of hydrogen and 5 ml of oxygen; (*c*) 10 ml of oxygen and 5 ml of hydrogen; (*d*) 20 ml of hydrogen and 20 ml of oxygen.

6. A chemist measured the composition of water by passing hydrogen over hot copper oxide as explained in the text. He obtained the following results:

Weight of copper oxide and tube before passing hydrogen through	70.6 g
Weight of copper oxide and tube after passing hydrogen through .	64.2 g
Weight of calcium chloride and tube at beginning of experiment .	110.8 g
Weight of calcium chloride and tube at end of experiment	118.0 g

Find (*a*) weight of oxygen present in water formed; (*b*) weight of water formed; (*c*) weight of hydrogen in water formed; (*d*) proportion in which the hydrogen and oxygen are present in the water.

OPTIONAL EXERCISES

1. Prepare the necessary apparatus, and explain to the members of the class just how you would proceed to determine the composition of water by the action of hydrogen on copper oxide.

2. Morley found the composition of water by directly weighing the hydrogen and oxygen that combine with each other to form water. The results of four trials are as follows:

Hydrogen Used	Oxygen Used	Hydrogen Used	Oxygen Used
(1) 3.2645 g	25.9176 g	(3) 3.8193 g	30.3210 g
(2) 3.2559 g	25.8531 g	(4) 3.8450 g	30.5294 g

(*a*) In each case calculate the ratio in which the hydrogen and oxygen combined to form water. (*b*) Calculate the average of the results.

CHAPTER XI

Carbon

[As Diamonds, a Costly Luxury; as Coal, a Cheap Necessity]

Carbon, the great chemical actor. We can all think of some great actor or movie star who plays many parts during his life on the stage or before the camera. He dresses in many costumes and acts now one part and now another. Carbon is the great dramatic artist among the elements. It plays the part of coal to drive our steam engines and warm our houses; it covers our larger cities with a cloud of smoke; it soils our clothes and gives us trouble with our automobile engines; it pleases us with diamond jewels. In the more complete disguise of chemical combination, it gives us more compounds than all other elements put together. It is worth while to know more about it.

Where carbon is found. In the uncombined state in nature, carbon is found in several forms. *Diamond* and *graphite* are very nearly pure carbon. The various kinds of *coal* contain more or less free carbon, together with a great number of other things.

But carbon is found much more abundantly in a great variety of compounds. Carbon dioxide (CO_2) is its most familiar gaseous compound. We breathe it from our lungs; plants feed upon it from the air; and in many places it flows from springs and gas wells. Natural gas, with which in some parts of the United States we heat our houses, and gasoline, which we use to run our automobiles, are largely compounds of carbon and hydrogen. It is a part of limestone, as well as of many other rocks. Our foods and our bodies contain large percentages of compounds of carbon. More than half the compounds that chemists know about are compounds of carbon. The study of these constitutes a special branch of chemistry called *organic chemistry.*

Carbon occurs in at least two allotropic forms, namely, the diamond and graphite, both of which are crystalline.

Crystalline carbon — the diamond. Most of the world's diamonds now come from the mines of South Africa. They

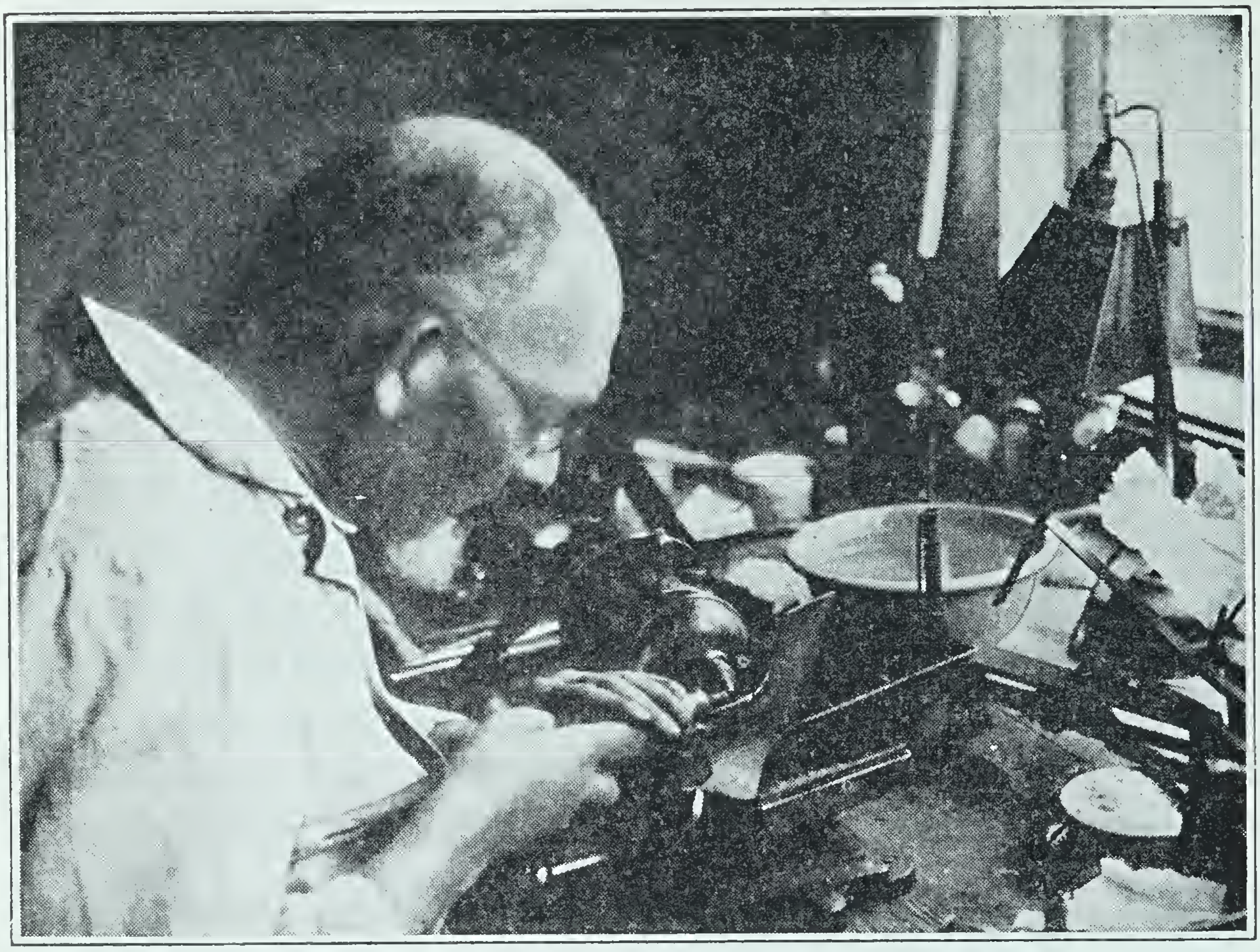


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FIG. 93. A skilled artist in Amsterdam, Holland, cutting the natural crystal diamond into shapes that give the most sparkle

are found in what are called "pipes" of a kind of clay formed by volcanic action, or in gravel washed from such formations. As found, the diamond does not look like a crystal but more like a pebble, and its surface is rough and discolored. To bring out the brilliancy of the gem, the natural crystals are ground, or "cut," into shapes that give the most sparkle. The cutting of diamonds requires great skill, and has been carried on very extensively in Holland and Belgium (Fig. 93).

The weight of the diamond is expressed in *carats*, a carat being equal to about 0.2 g. The word *carat* means the seed, or bean, of the carob tree. These beans may have been used formerly in weighing diamonds.

The largest of all known diamonds was the Cullinan, which was found in South Africa in 1905. The uncut stone weighed 3025$\frac{3}{4}$ carats (Fig. 94). The two largest gems cut from it are the largest cut diamonds in the world. The Jonkers diamond, found in 1935, weighed 726 carats. It has been estimated that there are today in the world more than

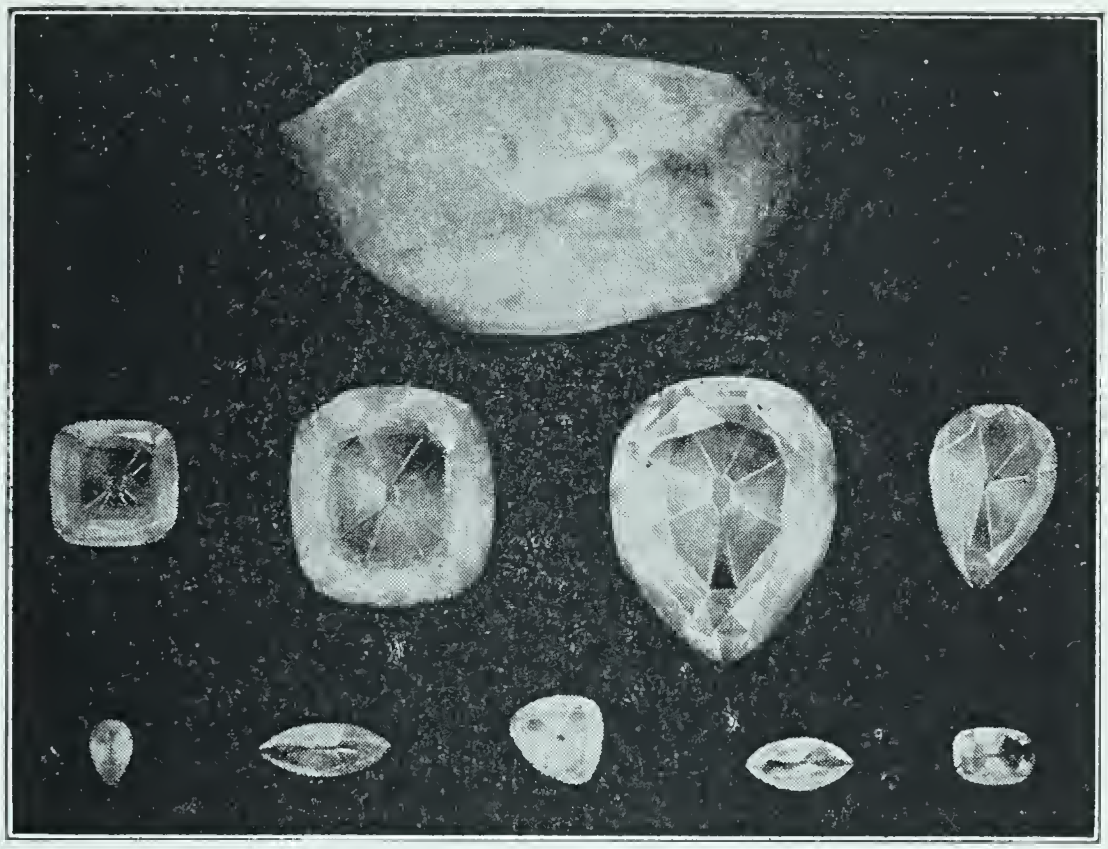

FIG. 94. The Cullinan diamond as originally found, together with the principal stones cut from it (one-half natural size)

fifty tons of cut diamonds, valued at something like seventy billion dollars. Dark-colored diamonds, although of no value as gems, are used to point core drills for cutting hard rocks, and for truing fine machine parts, especially the pistons of automobiles and airplanes.

The density of the diamond is 3.5, and, though brittle, it is one of the hardest of substances. Few chemical reagents have any action on it; but when strongly heated in oxygen or the air it blackens and burns, forming carbon dioxide:

$$C + O_2 \longrightarrow CO_2$$

Can diamonds be made in the laboratory? It is natural that chemists should try to make diamonds in the laboratory by crystallizing carbon. For a long time these attempts ended in failure, since graphite, and not diamonds, was always formed. Finally, in 1893, Moissan, a famous French chemist, succeeded in producing real diamonds, although they were too small to have any value as gems. He got them by dissolving carbon in melted iron and plunging the crucible containing the solution into water, as shown in Fig. 95. Under these conditions the carbon crystallized in the iron in the form of diamonds. The iron was then dissolved in hydrochloric acid, and little diamonds were found in the insoluble residue. Somewhat larger diamonds have been made since then in this same general way, but as yet there is no threat to the diamond mines. Fortunately a number of compounds nearly as hard as diamond are now made in electric furnaces for industrial uses. Most of these are compounds of carbon.

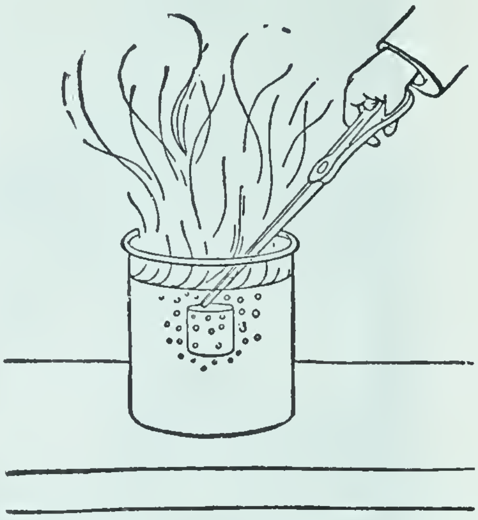

Fig. 95. Moissan's laboratory method of producing diamonds

Crystalline carbon — graphite. A second allotropic form of crystalline carbon, *graphite*, is found in large quantities, especially in Ceylon, Siberia, and in some parts of the United States, Mexico, and Canada. Large quantities of graphite are also manufactured commercially by heating hard coal to a high temperature in an electric furnace (Fig. 96). Prepared in this way it is purer than the natural product. Graphite is a shining black substance, very soft, and greasy to the touch. Its density is much less than that of the diamond, being about 2.25. It is used in the manufacture of "lead" pencils, electrodes, and crucibles, as

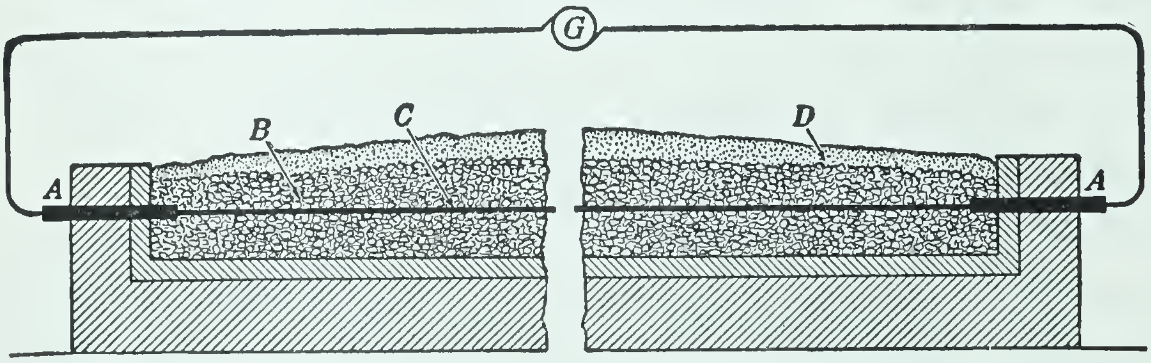

Fig. 96. Electric furnace for the commercial production of graphite

The process consists in heating hard coal in large electric furnaces about 40 ft in length, a longitudinal section of one of which is here shown. The electrodes *A* are made of graphite. The furnace is nearly filled with the coarse grains of coal *B*. Since the coal is a poor conductor of electricity, there is placed in the center of the charge a core, *C*, of carbon, which serves to carry the current through the charge. The charge is covered with a mixture, *D*, of sand and carbon (or similar materials), which serves to exclude the air. An electric current is supplied by the generator *G*. The current in passing through the charge meets with resistance sufficient to produce a high temperature. Under the influence of the intense heat the carbon is changed into graphite. Prepared in this way, the product is uniform in composition and free from grit and is therefore superior to the natural product for most purposes a lubricant instead of grease, and (in the form of a polish or a paint) as a protective covering for iron (stove polish).

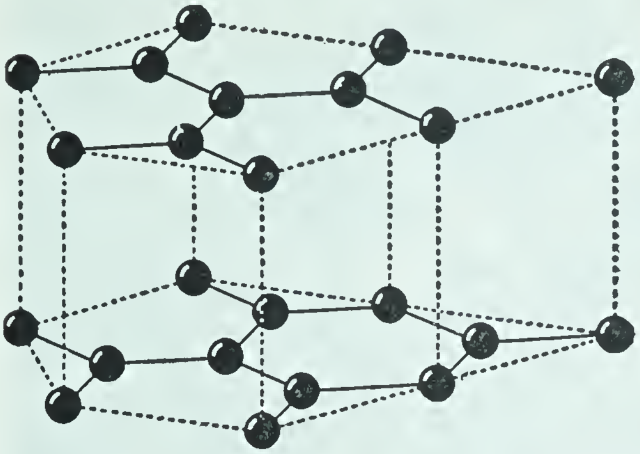

Fig. 97. The arrangement of the carbon atoms in graphite

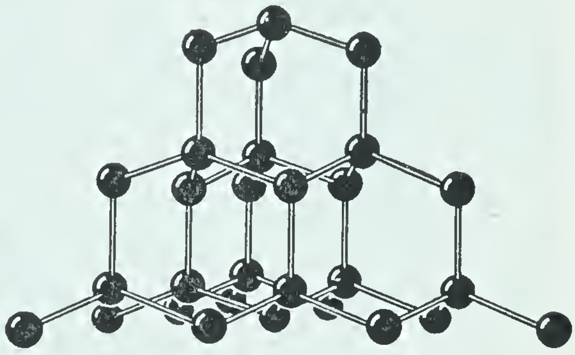

Fig. 98. The arrangement of the carbon atoms in the diamond

In graphite the carbon atoms are arranged in flat rings, piled one on another like a stack of plates (Fig. 97). In the diamond they are at the four corners of a tetrahedron, and are packed together in very compact form (Fig. 98).

Other forms of carbon. In addition to the diamond and graphite, free carbon is the chief constituent of a number of products, such as coal and charcoal (described below). It was formerly thought that the free carbon present in these products was amorphous, but the more accurate methods now known indicate that it, like the diamond and graphite, is also crystalline. Most of the compounds present in plants and animals contain carbon; and, as a rule, these yield carbon when heated in the absence of air.

1. ***Coal and coke.*** The various forms of coal (Fig. 99) were formed from vast accumulations of vegetable matter. In *hard* coal, or *anthracite*, nearly all the carbon is in the uncombined state. In *soft*, or *bituminous*, coal a considerable part of the carbon is combined with one or more of the elements hydrogen, oxygen, nitrogen, and sulfur.

When soft coal is heated in the absence of air, complex chemical changes take place which yield many useful compounds of carbon. These compounds are given off in the form of gases and vapors, while the mineral matter and free carbon stay behind as solids. This process of decomposition in the absence of air is called *destructive distillation.* Ordinary distillation (p. 118) does not bring about a chemical change.

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FIG. 99. Mining coal in a typical mine

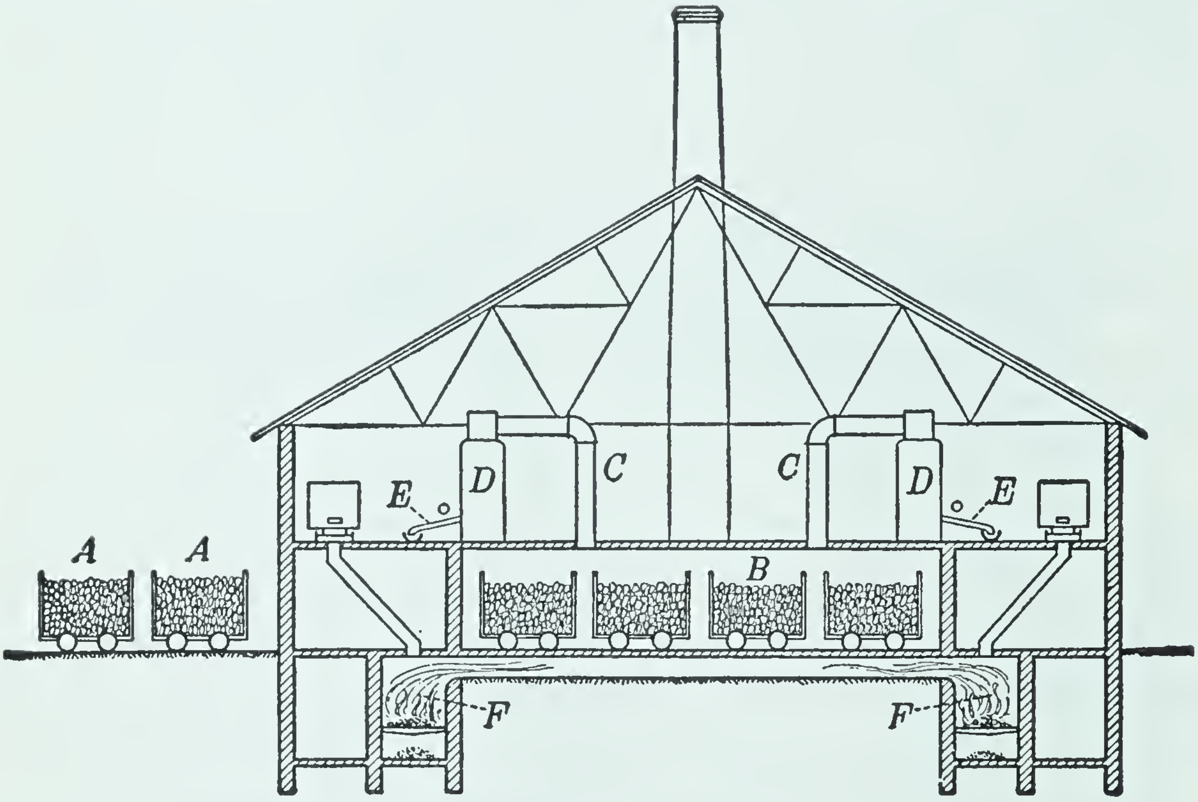


FIG. 100. Drawing of a plant for the production of charcoal by the modern method

Iron cars *A*, *A* are loaded with wood and run into a low, narrow iron room, or *retort*, *B*. The retort is then made airtight and heated slowly for twenty-four hours by the fires *F*, *F*. The volatile products escape through the pipes *C*, *C* and then pass into the condensers *D*, *D*. Here those portions which are liquid at ordinary temperatures, such as *wood alcohol* and *acetic acid*, are condensed, while the gaseous products are led back and burned in the fires *F*, *F*. When all the volatile matter has been expelled in this way, the cars containing the charcoal are run into cooling chambers, and their place in the retort is taken by other cars loaded with wood

The gases and vapors which escape in the destructive distillation of coal are called *volatile* matter; the solid that remains is *coke.* In hard coal the volatile matter averages from 5 per cent to 8 per cent, while in soft coal it averages from 30 per cent to 35 per cent. When coal is burned, the mineral matter present is left as ash.

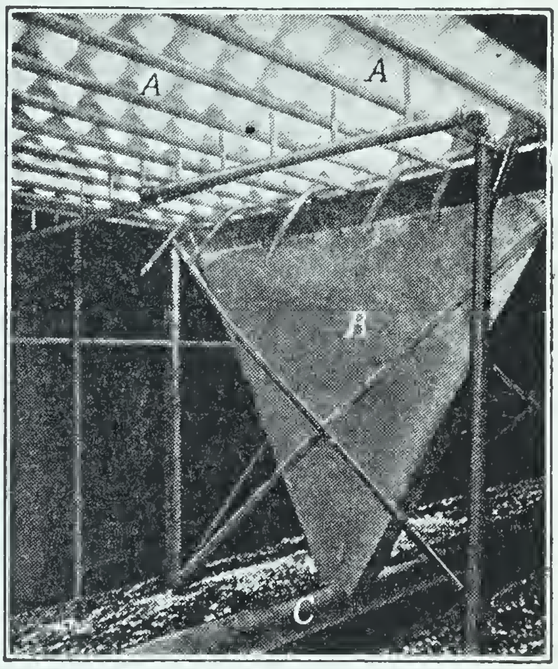


Fig. 101. Making carbon black by the partial burning of natural gas

The flames *A* strike against a cold metal plate. The unburned carbon deposited on this plate is scraped into the compartment *B* and drawn by an air current into the tube *C*, which leads to storage containers

2. ***Charcoal.*** This is made from wood, just as coke is made from coal. The volatile matter formed and driven off by the heat contains many valuable substances, such as *methanol* (wood alcohol) and *acetic acid* (present in vinegar), which are obtained commercially in this way as well as by more modern synthetic methods. Formerly much of this volatile matter was allowed to escape. But at present a large amount of charcoal is prepared in such a way that the volatile matter is condensed and saved (Fig. 100), as in the heating of coal for making coke. Both charcoal and coke are used as fuels, and are especially useful in the reduction of metals from their oxides, as will be explained later.

3. ***Boneblack, or animal charcoal.*** This is made by heating bones and animal refuse in the absence of air. It consists of calcium phosphate and very finely divided carbon, and is especially useful as a filter for removing coloring matter in the refining of various products such as sugar.

4. ***Carbon black, or lampblack.*** Carbon black is the soot made by burning natural gas or fuel oil under special conditions. The air supply is limited, and the smoky flame is directed upon the under side of a cold metal plate on which the soot deposits (Fig. 101). Made in this way (or in some similar way) it is a very fine black powder. It is called carbon black or lampblack, according to the way it happens to

be made. When first made the particles are so small and enclose so much air that a cubic foot weighs only four pounds.

About 80 per cent of the total production is used in the rubber of automobile tires; for no other substance gives the tire so much strength and resistance to wear and hard bumps. It has been the pigment of black inks since the days of the early Egyptians and Chinese, and all the books since the invention of the printing press have been printed in lampblack inks. Benjamin Franklin made his own black ink for his press.

Physical properties of carbon. While the various forms of carbon differ in many properties, especially in hardness, they are nevertheless all odorless, tasteless solids, insoluble in water and in all other solvents except some molten metals. Even in the intense heat of the electric arc, carbon does not melt, though it vaporizes to some extent.

Carbon has great adsorbing power. All varieties of finely powdered carbon (usually called amorphous) have the property of taking up, or *adsorbing*, many gases, as well as other substances that give objectionable color, odor, or taste to many raw materials. For this reason crude sugar solutions are filtered through boneblack. Carbon of high adsorptive power is called *activated* carbon.

This adsorptive power depends largely on the extent of carbon surface; and this in turn depends on the animal or vegetable material from which the carbon is made. When made from coconut shells or peach stones, 1 volume of carbon will adsorb about 250 volumes of air. It has been estimated that 1 cubic inch of a good activated carbon will have about 20,000 square yards of surface.

An important use of activated carbon is in making gas masks (Fig. 102). These were invented during World War I to protect troops from poisonous gases. Now they are of great value as a protection against poisonous gases that occur in many ways — during fires, in mines, and in certain industries.

Chemical conduct. At ordinary temperatures carbon is very inactive, but at higher temperatures it combines directly with most of the elements. Because of its strong affinity for oxygen it is an excellent reducing agent. We could not have iron or steel without carbon. Its compounds with the metals are called *carbides*. One of the most important of these is *calcium carbide* (CaC_2), which is used in making acetylene.

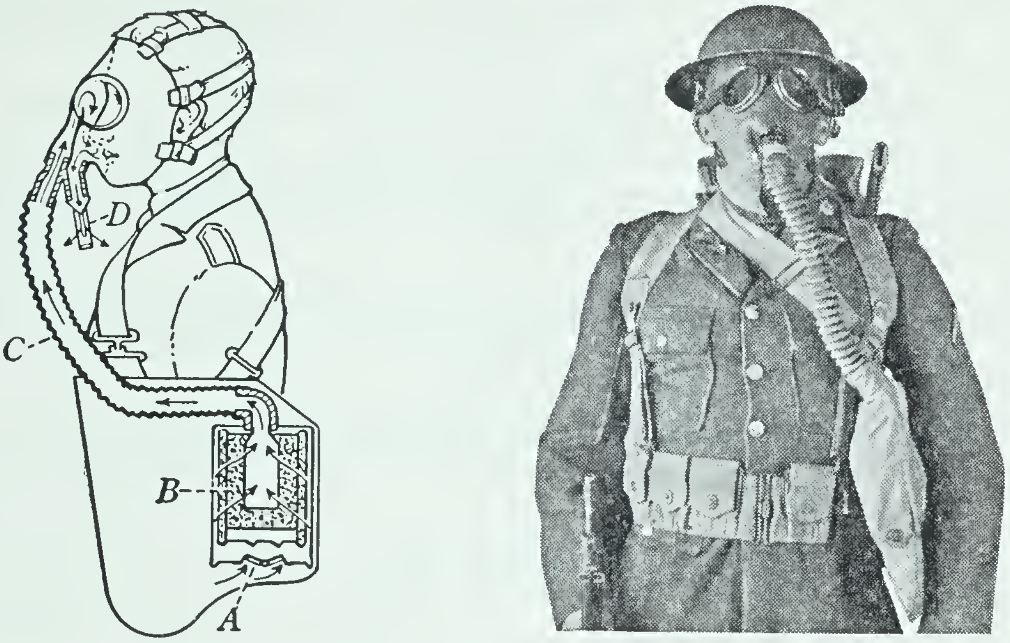


FIG. 102. The drawing at the left shows the parts of a gas mask. At the right is a soldier equipped with the mask

The air enters the mask at *A* and passes through the canister *B*, filled with activated carbon and other chemicals that remove the poisonous gases. The purified air then passes through the tube *C* and is inhaled. The exhaled air escapes at *D*

When carbon (or a substance containing it, such as wood or coal) burns, the element combines with oxygen to form either *carbon dioxide* (CO_2) or *carbon monoxide* (CO), depending chiefly upon the amount of oxygen present. Both of these oxides are colorless gases and will be described in the next chapter.

Uses of carbon — summary. The chief use of carbon is for fuel, to furnish heat and power for all the requirements of civilization. An enormous quantity of carbon in the form of coal, coke, and charcoal is used as a reducing agent in getting the various metals from their ores. Carbon black is used for making motorcar tires, indelible ink, printer's ink, paints, and black varnishes, while boneblack and charcoal are used in filters. Activated charcoal is used in refining various products and in making gas masks.

CHAPTER SUMMARY IN QUESTION FORM

1. Mention five different substances that are pure carbon or contain free carbon.

2. (*a*) Which of the substances given in answer to question 1 is costly? (*b*) Which is the most useful?

3. Name some of the common compounds of carbon that occur in nature.

4. How do the diamond and graphite differ in (*a*) color? (*b*) density? (*c*) hardness? (*d*) uses?

5. (*a*) Who was the first to prepare diamonds in the laboratory? (*b*) Describe the process.

6. Draw a diagram of an electric furnace and show how graphite is produced in such a furnace.

7. What name do we give to the different states of the same element, such as that of the diamond and graphite?

8. (*a*) Name the different varieties of coal. (*b*) How do they differ in composition and properties?

9. What changes take place when coal is heated (*a*) in the presence of air? (*b*) in the absence of air?

10. What name is given to the heating of such substances as coal, wood, and bones in the absence of air?

11. Suppose you heat each of the following substances in the absence of air: (*a*) soft coal; (*b*) wood; (*c*) bones. What product is left in each case?

12. (*a*) What forms of carbon are found in nature? (*b*) What forms are produced in the laboratory? (*c*) What forms are both found in nature and produced in the laboratory?

13. Describe the preparation of each of the following substances: (*a*) coke; (*b*) charcoal; (*c*) boneblack; (*d*) carbon black.

14. In making charcoal, name two products formed in addition to the charcoal.

15. (*a*) What property of carbon makes it useful in gas masks? (*b*) Name the commercial form of carbon that possesses this property to a marked degree.

16. Does carbon combine readily with other elements (*a*) at ordinary temperatures? (*b*) at higher temperatures?

17. What name is given to the compounds composed of (*a*) carbon and the metals; (*b*) carbon and oxygen?

18. Give the various uses of each form of carbon.

THOUGHT QUESTIONS

1. Why do we speak of carbon as an inactive element when it combines with most of the elements?

2. Calculate the approximate weight of carbon present in your body.

3. Both carbon and hydrogen have what important property in common?

4. Should you expect the charcoal in a gas mask to lose its effectiveness with use?

5. Carbon has a great affinity for oxygen; yet we paint iron structures with carbon paints to protect them from the oxygen of the air. Explain.

6. We are willing to pay much more for some varieties of coal than for others. Why?

7. (*a*) Is there anything in the appearance of the diamond that would lead you to think it was composed of carbon? (*b*) How do you suppose that chemists first discovered that the diamond is really pure carbon?

8. (*a*) What is the "lead" used in making lead pencils? (*b*) Why is it called lead?

9. What proof have we that such widely different substances as the diamond, graphite, and anthracite are all forms of free carbon?

10. Which of the forms of carbon would give the least per cent of ash?

11. Many of the so-called "diamonds" are simply cut glass. Suggest a way of telling these from real diamonds.

12. If you drop a little sugar on a hot stove, the sugar turns black and finally disappears. Explain.

OPTIONAL EXERCISES

1. Design a "carbon tree" in which the trunk is carbon, the main limbs are the different forms of carbon, and the products formed by their combustion are the secondary limbs.

2. Build and exhibit to the class a model of a furnace for making graphite. The following are some suggested materials, since they are easily secured: empty chalk box; two crayons; pieces of coal; core of a lead pencil; sand.

CHAPTER XII

The Two Oxides of Carbon

[The One Puts Out Fire; the Other Burns]

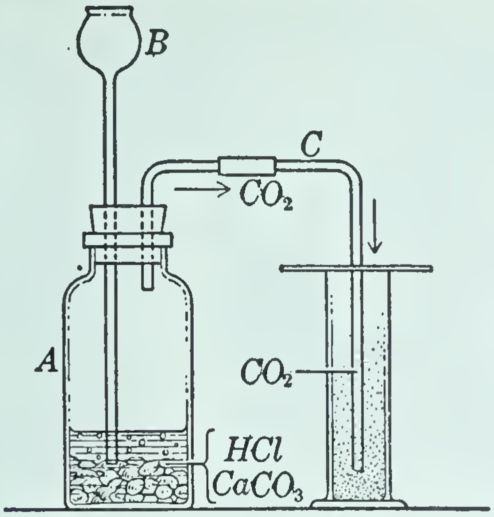
One atom of oxygen makes a world of difference. The two well-known oxides of carbon have very simple formulas. The one (carbon dioxide) is CO_2; the other (carbon monoxide) is CO. These formulas do not look very different. The first has one more atom of oxygen than the other; but what a difference this makes! The one oxide is often used to put out fires; the other burns, and is one of the constituents of commercial fuel gases. The one is in our lungs all the time and is breathed out with every breath; the other is a deadly poison that kills many people each year. The one is a heavy gas; the other, lighter than air. The one is not hard to liquefy; the other, one of the most difficult.

Chemistry is full of surprises. One of the most wonderful of them is the difference just one atom in a molecule sometimes makes.

I. CARBON DIOXIDE

Carbon dioxide (carbonic acid gas) (CO_2). Carbon dioxide is often called *carbonic acid gas.* It is a colorless and odorless gas and is formed whenever carbon itself or any of the common fuels burns in oxygen or air. It is also formed in such processes as fermentation and the decay of animal and vegetable matter. Large quantities escape from volcanoes and crevices in the earth. It is present in the open air to the extent of about 3 parts in 10,000 by volume. When we study the atmosphere, we shall see that this relatively small percentage is essential to the life of all plants; so it indirectly supplies us with our food. It is estimated that there is about 35 times as much carbon dioxide dissolved in the water of the oceans as is present in the atmosphere.

Preparation. In the laboratory we get carbon dioxide by the action of hydrochloric acid on the compound called calcium carbonate ($CaCO_3$). This is found in nature in many



The figure shows a simple apparatus for preparing carbon dioxide by the action of hydrochloric acid on marble (calcium carbonate). Small pieces of marble are placed in the bottle *A*, and the acid is added through the funnel tube *B*. The carbon dioxide set free escapes through the exit tube *C*, and, being heavier than air, collects in the cylinder, pushing out the air. Since it is not very soluble in water, it may also be collected over water (as are hydrogen and oxygen)

Fig. 103. The preparation of carbon dioxide

different substances, such as shells, coral, and limestone. Marble is nearly pure calcium carbonate, and is the material most often used in getting carbon dioxide. When hydrochloric acid and marble are brought in contact with each other (Fig. 103), calcium chloride ($CaCl_2$), water, and carbon dioxide are formed, as shown in the equation

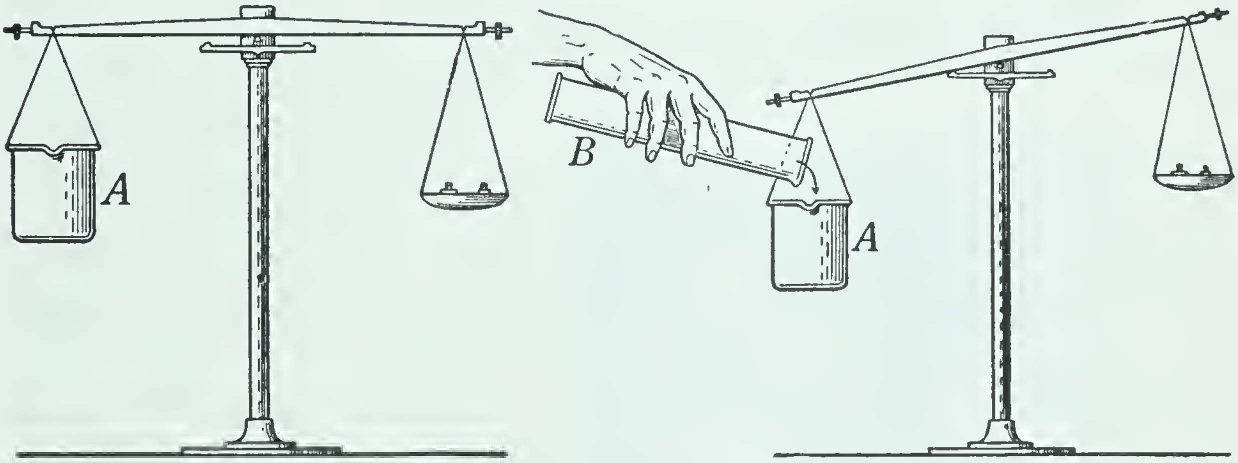


Fig. 104. Carbon dioxide is heavier than air

The drawing at the left shows a beaker counterpoised with weights. The drawing at the right shows the result when carbon dioxide is poured into the beaker

$$CaCO_3 + 2\,HCl \longrightarrow CaCl_2 + H_2O + CO_2\uparrow$$

An arrow placed after the formula of a compound and pointing up (as $CO_2\uparrow$) signifies that the compound is a gas.

On a large scale, carbon dioxide is prepared by burning coal or coke. The resulting carbon dioxide is then separated from the other gases formed in the combustion of the fuel,

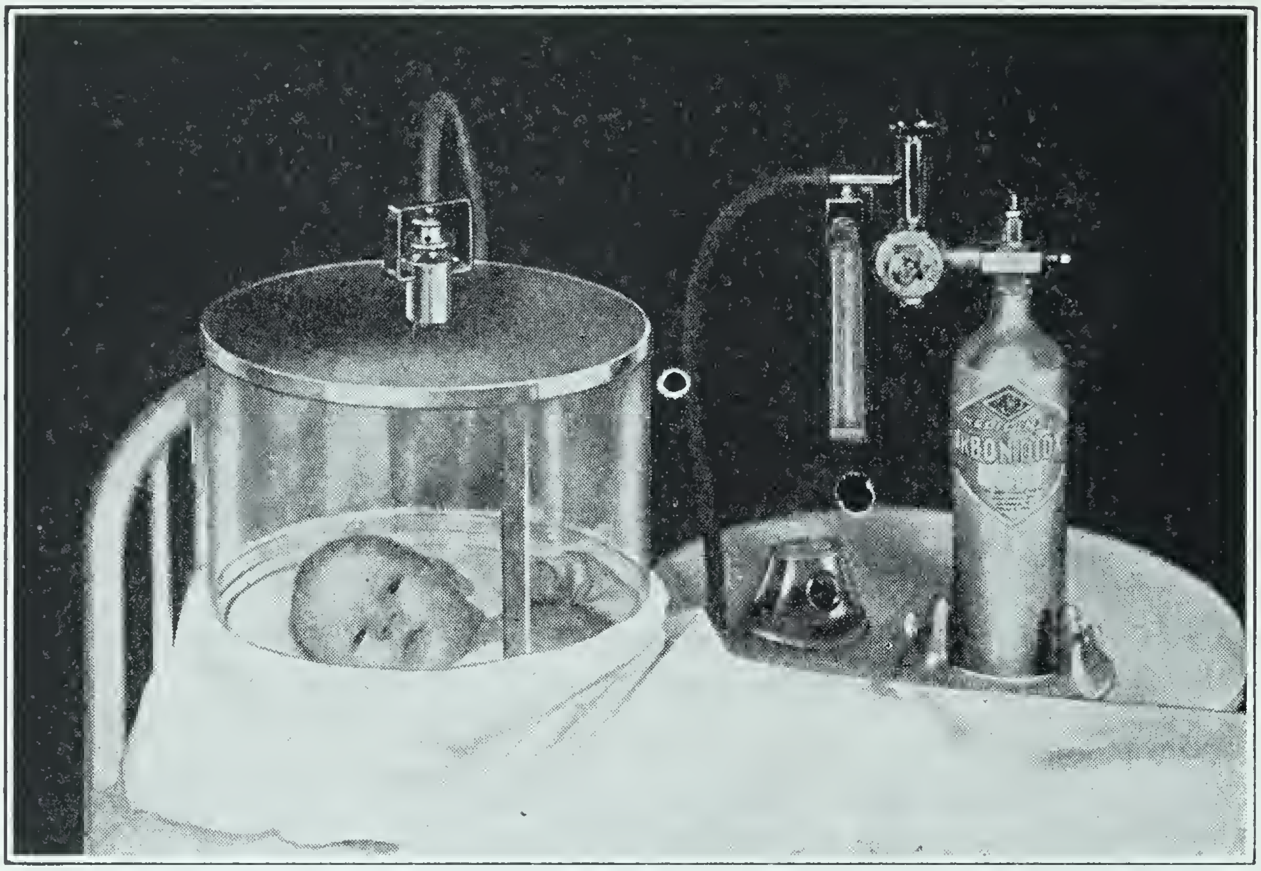


Fig. 105. Oxygen (or air) with added carbon dioxide administered to relieve difficulty in breathing

and from the nitrogen and excess oxygen of the air. In some places the nearly pure gas flows from gas wells. The pure carbon dioxide is then pumped into strong steel cylinders and in this form is sold on the market.

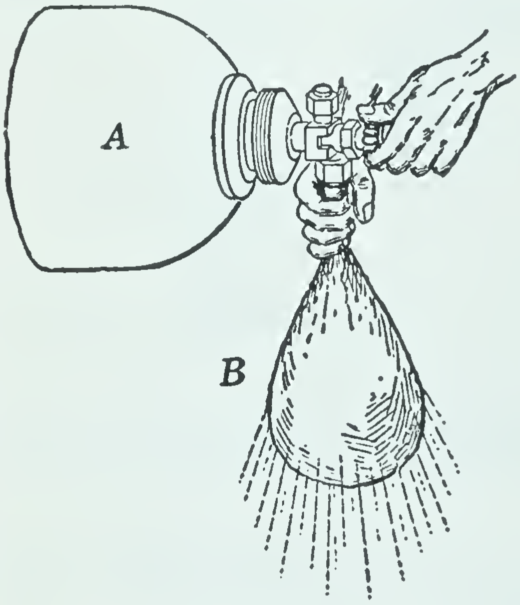


Fig. 106. Making "dry ice"

Liquid carbon dioxide from the cylinder *A* runs into the loose bag *B*, and evaporates so fast as to leave solid carbon dioxide in the bag

Properties of carbon dioxide. Carbon dioxide is a heavy gas, about 1.5 times as heavy as air. Because of its weight, it can be poured like water from one vessel into another (Fig. 104). It sometimes escapes from cracks in the earth faster than it can diffuse into the air, and so tends to collect in deep wells or in caves.

Under ordinary conditions of temperature and pressure (that is, 15° and a pressure of 1 atmosphere) 1 volume of water dissolves about 1 volume of the gas. With increasing pressure correspondingly larger volumes of gas are dissolved (p. 70). If the pressure on

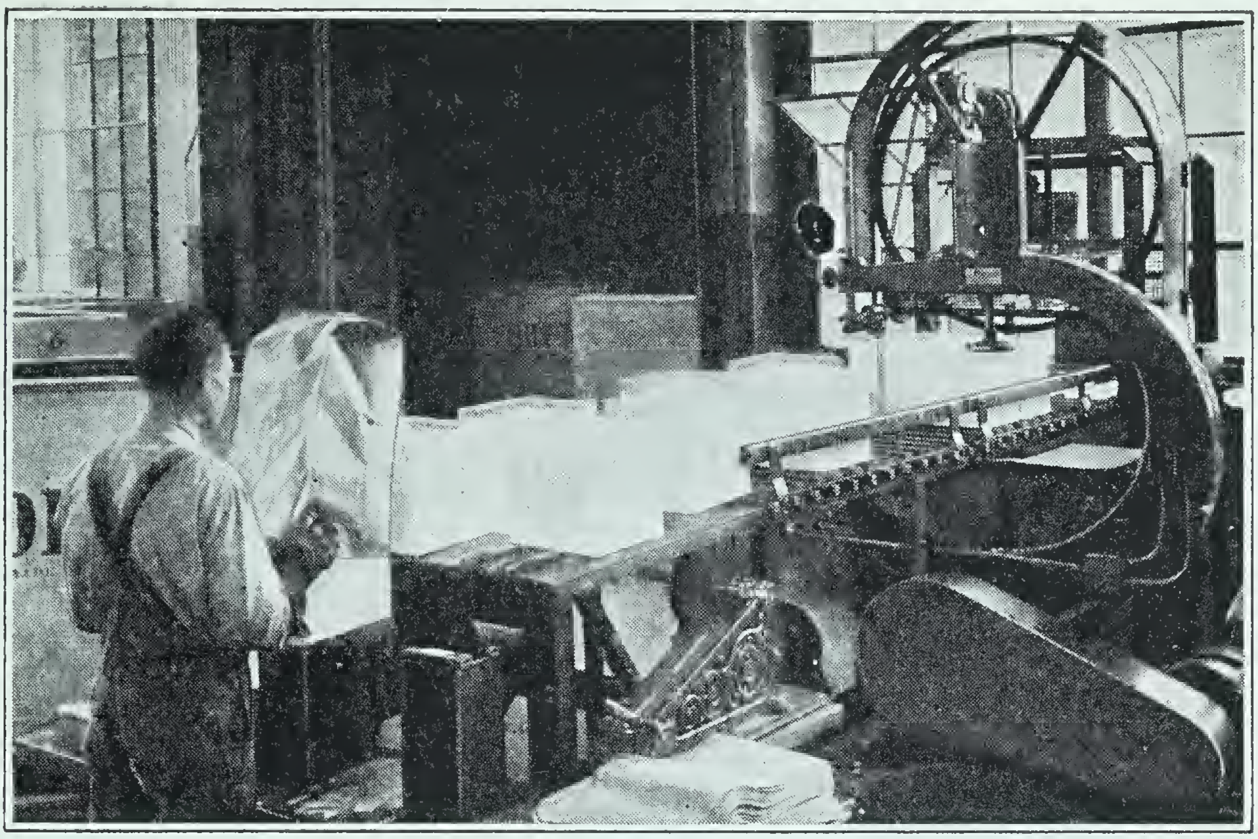


Fig. 107. Solid carbon dioxide (known as "dry ice") being sawed by machinery into pieces of a size suitable for use as a refrigerant

such a saturated solution is taken off, most of the gas escapes with effervescence (Fig. 46), as in the case of soda water or pop. Carbon dioxide is not thought of as a poisonous gas, but a high percentage in the air is known to be injurious or even fatal in its effects.

When oxygen is used in cases of pneumonia (p. 94), or of smothering or poisoning by other gases, a little carbon dioxide is often mixed with the oxygen (see Fig. 105). It has been found that breathing is much helped by it.

Liquid and solid carbon dioxide. When carbon dioxide is forced into

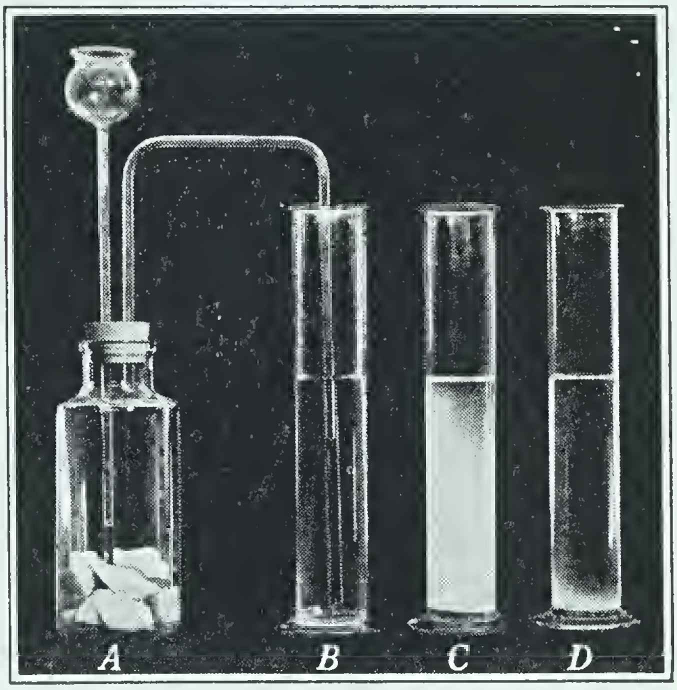


Fig. 108. The action of carbon dioxide on a solution of calcium hydroxide (lime water)

The carbon dioxide generated in *A* bubbles through the lime water in *B*. The calcium carbonate formed, as shown in *C*, gradually settles to the bottom of the cylinder, as shown in *D*

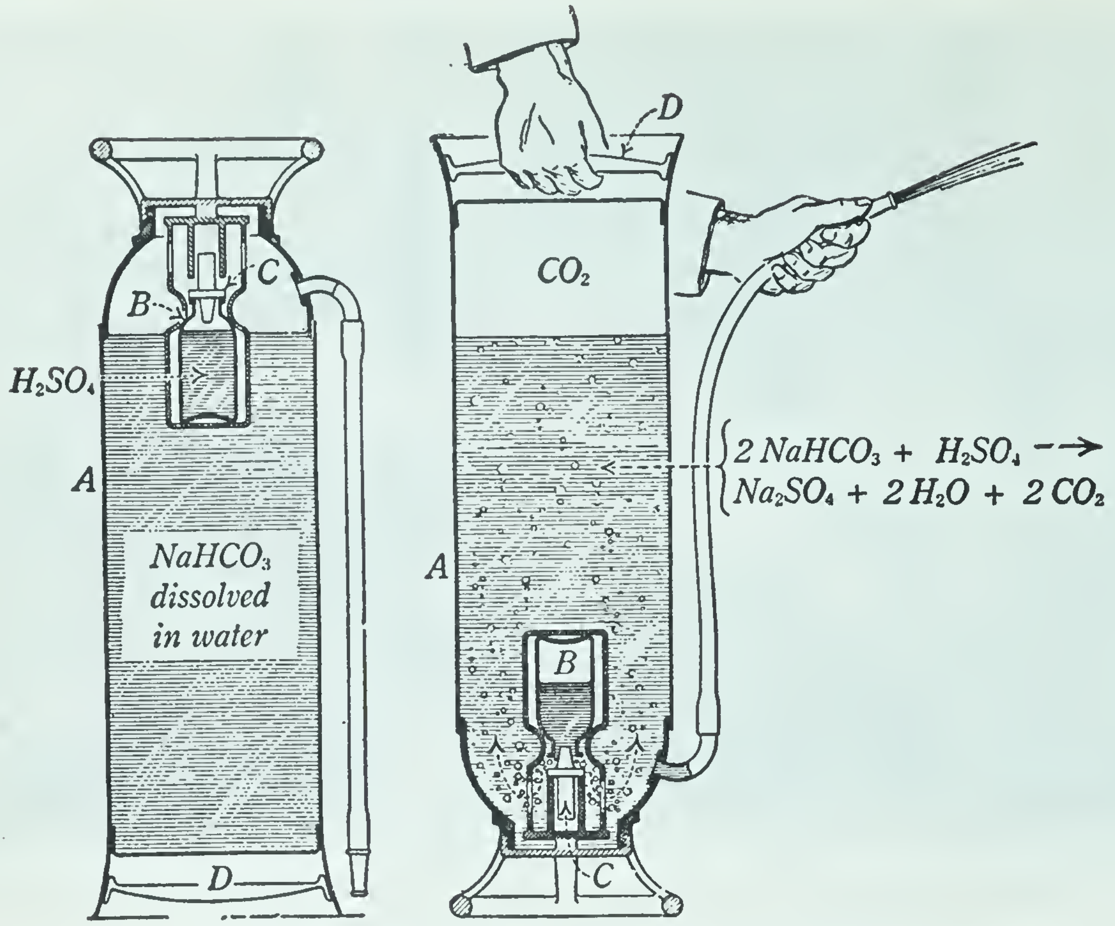

D
C
B
H_2SO_4
A
$NaHCO_3$ dissolved in water
D
CO_2
$2\,NaHCO_3 + H_2SO_4 \rightarrow$
$Na_2SO_4 + 2\,H_2O + 2\,CO_2$
A
B
C

FIG. 109. One form of portable fire extinguisher

The liquid is a solution of sodium bicarbonate ($NaHCO_3$) in water, contained in a metal cylinder. The bottle *B* contains sulfuric acid. In case of fire the apparatus is grasped by the handle *D* and inverted as shown in the second figure. The stopper *C*, resting on the top of the bottle *B*, drops down onto the support. The acid flows slowly from the bottle and at once reacts with the sodium bicarbonate, generating carbon dioxide (see equation on the figure). Some of the gas thus generated dissolves in the water, while the remainder forces the water out through the nozzle. While the volume of water so obtained is not large, it is much more effective as a fire extinguisher than a stream of ordinary water, because the carbon dioxide present helps to smother a fire

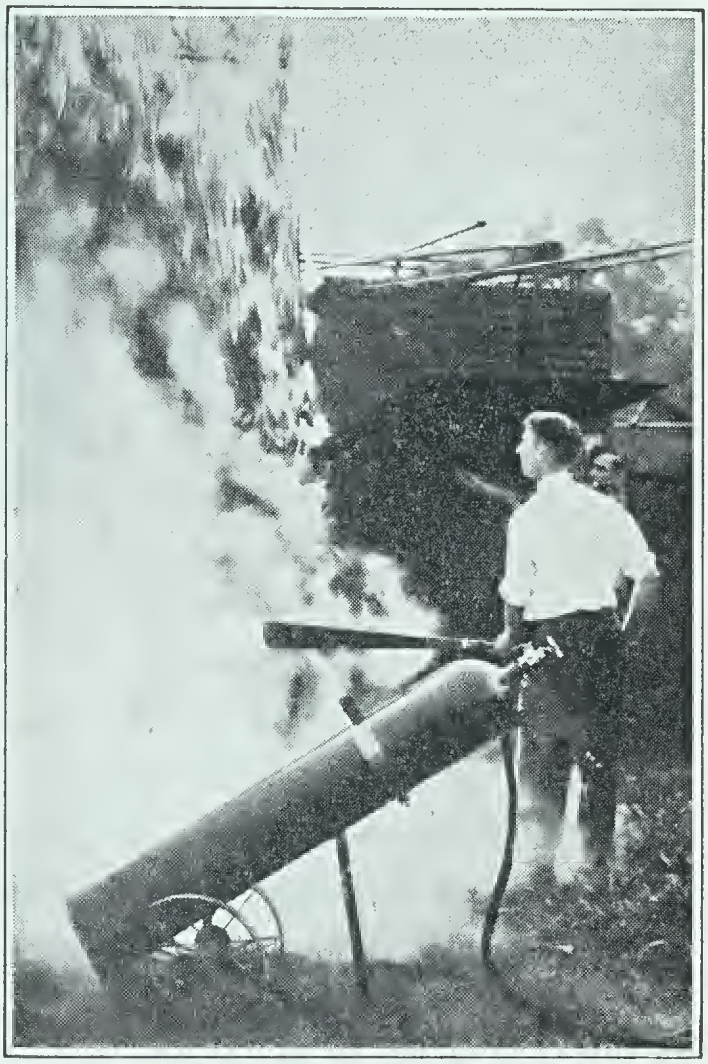
a strong steel cylinder at ordinary temperatures until the pressure reaches 52 atmospheres, any additional gas condenses to a colorless liquid. If the pressure on this liquid is suddenly removed (Fig. 106), the liquid evaporates very rapidly, and the heat absorbed in the process (p. 59) is so great that some of the liquid is frozen into a white solid resembling snow. In the open air this solid slowly evaporates without melting, keeping at a temperature of about −72° as long as it lasts.

Solid carbon dioxide is now produced in quantities and sold at a low price on the market as "dry ice" (Fig. 107). It is a good refrigerant, and is used widely throughout the world for this purpose, especially in shipping ice cream and perishable foods. It has the advantage over ice that there is no water to dispose of, it is much lighter than ice, and the gaseous carbon dioxide formed by its evaporation is a very good preservative.

How carbon dioxide acts. Carbon dioxide is neither combustible nor a supporter of combustion. When it is bubbled through a clear solution of calcium hydroxide ($Ca(OH)_2$) (ordinary *limewater*), the solution soon becomes cloudy (Fig. 108). This is due to the formation of calcium carbonate, which is insoluble in water and slowly precipitates:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3\downarrow + H_2O$$

This reaction with calcium hydroxide is used as a simple test for carbon dioxide.



Walter Kidde & Co.

Fig. 110. Another form of fire extinguisher

A fine spray of gaseous and solid carbon dioxide escapes from the metal cylinder, in which it is stored under great pressure

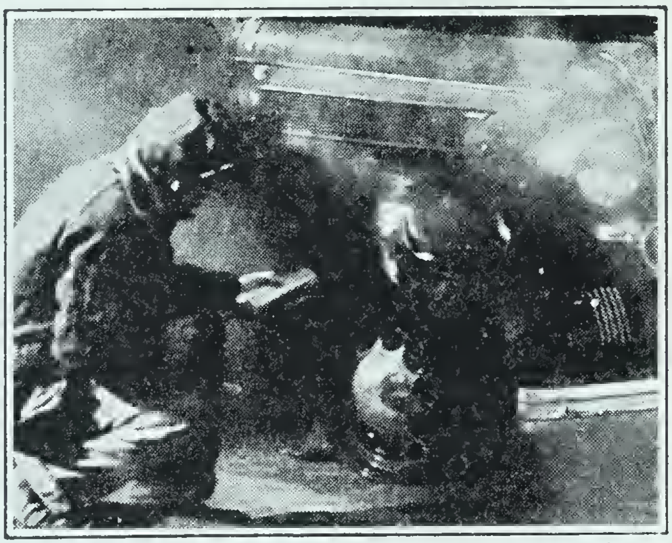
When bubbled through water a small percentage of the gas unites with the water, forming a very unstable soluble compound, H_2CO_3, called *carbonic acid*:

$$H_2O + CO_2 \longrightarrow H_2CO_3$$

Carbon dioxide has important uses. The carbon dioxide in the air is a food for plants, as will be shown in the chapter on the atmosphere. Commercially it is used chiefly in the manufacture of soda water and similar beverages, in making "dry ice," and as a fire extinguisher. A burning candle is extinguished in air which contains as little as 2.5 per cent of carbon dioxide. This seems strange, since there would appear to be plenty of oxygen left in the air to support combustion.

Portable fire extinguishers. There are several types of portable fire extinguishers. The one shown in Fig. 109 is simply a device for generating carbon dioxide under pressure. In Fig. 110 carbon dioxide compressed in steel cylinders is being used.

The type of extinguisher that is shown in Fig. 111 is a smaller metal cylinder filled with a liquid composed chiefly of carbon tetrachloride (CCl_4) and fitted with a sort of piston for forcing the liquid out in case of fire. The liquid is not combustible and is easily volatile, forming a heavy vapor. So when it is thrown onto a fire, it quickly evaporates, and the heavy vapor surrounds the burning body and prevents the oxygen of the air from getting at it. Other forms of fire extinguishers will be described in connection with the reactions that take place in their use.



Acme

Fig. 111. Extinguishing an automobile fire with carbon tetrachloride

II. CARBON MONOXIDE

Carbon monoxide (CO). This compound resembles carbon dioxide in being a colorless, odorless gas. It differs from it in being inflammable and very poisonous. It burns with a pale-blue flame, forming carbon dioxide:

$$2\,CO + O_2 \longrightarrow 2\,CO_2$$

Because of its strong affinity for oxygen, it is a good reducing agent. For example, if we pass the gas over hot copper oxide, we get metallic copper and carbon dioxide:

$$CuO + CO \longrightarrow Cu + CO_2 \uparrow$$

In the laboratory, carbon monoxide is usually prepared by heating formic acid (H_2CO_2) with sulfuric acid:

$$H_2CO_2 \longrightarrow H_2O + CO \uparrow$$

Sulfuric acid is not shown in the equation because it merely aids in the reaction by combining with the water that is produced.

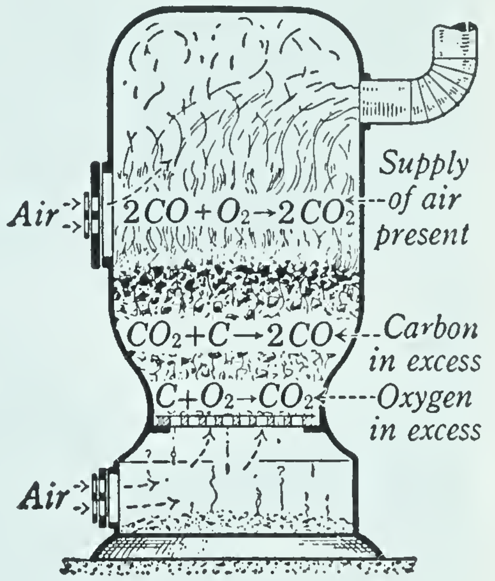

Air
$2CO + O_2 \rightarrow 2CO_2$
Supply of air present
$CO_2 + C \rightarrow 2CO$
Carbon in excess
$C + O_2 \rightarrow CO_2$
Oxygen in excess
Air

Fig. 112. Carbon monoxide

Formation of carbon monoxide when hard coal is burned in a stove

Carbon monoxide is also formed whenever coke, or hard coal, is used as a fuel in a furnace or stove, such as pictured in Fig. 112. In such stoves the carbon dioxide at first formed rises through the red-hot coals, and is *reduced* to carbon monoxide

$$CO_2 + C \longrightarrow 2\,CO\uparrow$$

If there is a good air draft, and not too much cold fuel on top of the hot coals, this carbon monoxide burns above the coal with a pale-blue flame familiar to everyone who has looked in at the furnace door. If the supply of air is limited, a part of the monoxide goes up the chimney as one of the products of combustion.

Carbon monoxide is also formed when gas is burned in stoves and grates and the flame is allowed to strike against any cold object, such as a kettle of water or even the stove or grate itself, before it gets hot. Carbon monoxide has a high kindling temperature (p. 92), and the flame is easily chilled to a point below the kindling temperature of this oxide. So any of it formed in this way escapes into the room unless suitable pipes are arranged for conducting it into the chimney

Many persons die each year from breathing carbon monoxide. Carbon monoxide is very poisonous, because it combines with one of the constituents of the red corpuscles of the blood and makes it unable to carry oxygen to the body cells. Recent experiments have proved that "1 part of the gas in 1000 parts of air breathed for one-half hour can render a healthy, inactive man unconscious; if active, a man breathing this dilution will succumb sooner." It is also a very treacherous poison, because it has no odor and gives

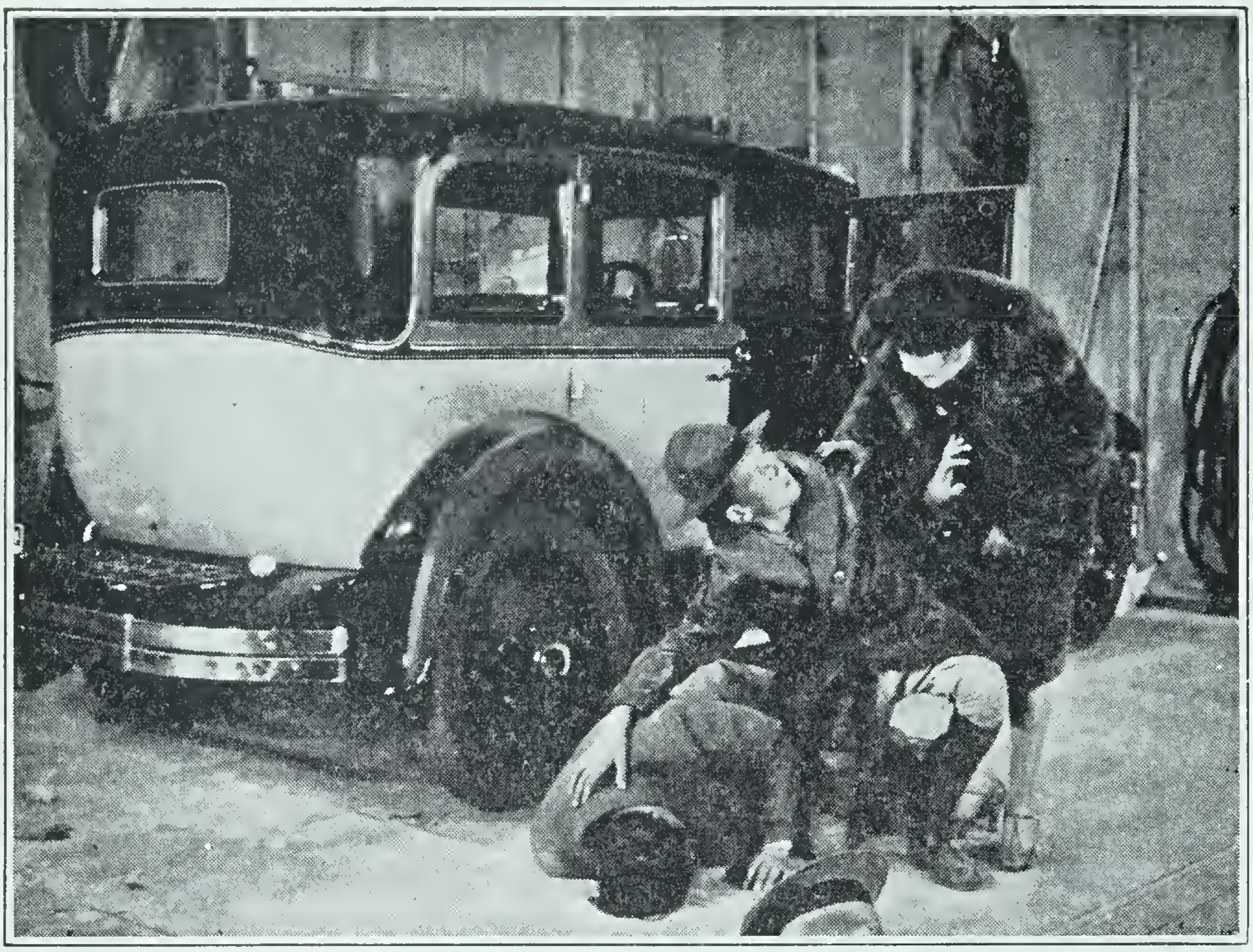


Fig. 113. Carbon monoxide poisoning in a closed garage

The boy is about to apply first-aid treatment and is telling his mother to call a physician. (Courtesy of the United States Bureau of Mines)

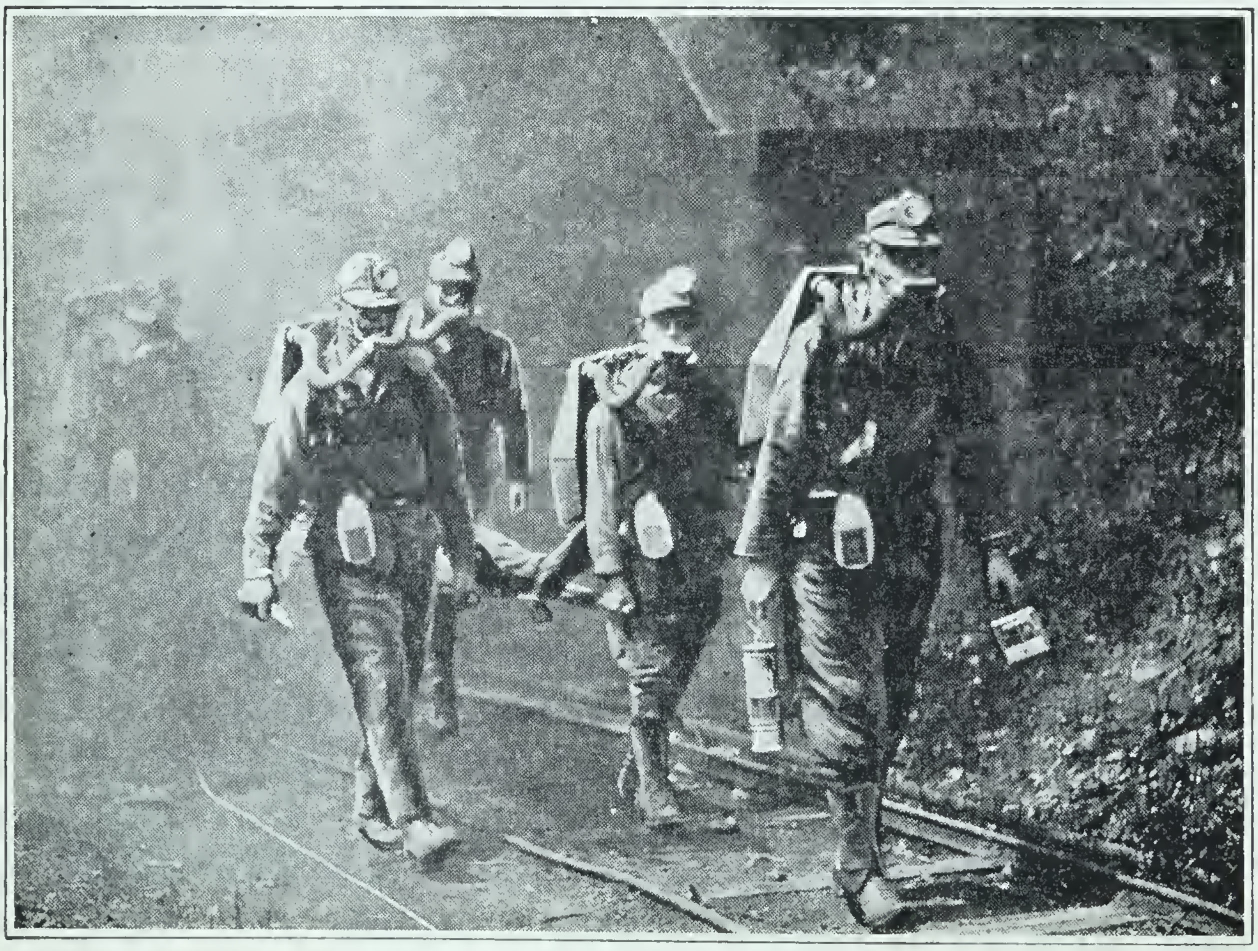


Fig. 114. Mine rescuers provided with gas masks and living canaries

no warning of its presence. A person breathing it feels no ill effects but suddenly collapses.

In order to avoid poisoning by carbon monoxide it is of the greatest importance that all stoves and grates be provided with suitable chimney connections and that these connections be kept open. If this is not done, any carbon monoxide formed may escape into the air of the room and poison anyone breathing this air. Many lives are lost each year owing to defective gas stoves and to stoves with no chimney connections.

The risk from automobile exhausts. Another risk of poisoning from carbon monoxide is in breathing the air in a closed garage where an automobile engine is allowed to run. The exhaust gases of such engines contain from 4 to 12 per cent of carbon monoxide, so that the air in such a garage soon becomes very dangerous. *Each year many a person loses his life by working in a closed garage in which an engine is running* (Fig. 113).

It is interesting to note that birds are very easily poisoned by carbon monoxide. In mine explosions carbon monoxide is always formed, and rescuers sometimes carry canaries with them, the death of the birds warning the rescuers of their own peril (Fig. 114).

CHAPTER SUMMARY IN QUESTION FORM

1. Give the name and formula of each of the oxides of carbon.

2. (*a*) Which of the oxides of carbon is formed when carbon burns in air? (*b*) Under what conditions is this oxide changed into the other oxide?

3. Answer the following questions in reference to carbon dioxide: (*a*) By what other name is it known? (*b*) Name three natural sources of the gas. (*c*) Account for the fact that it can be poured from one vessel into another like water. (*d*) What property of the gas is important in making soda water? (*e*) What happens to the gas (1) when subjected to very great pressure? (2) when released from such pressure suddenly? (*f*) Name the chemicals used in the preparation of the gas in the laboratory, and write the equation for their reaction with each other.

4. What would be the effect of removing all the carbon dioxide from the atmosphere?

5. Tell what takes place (*a*) when carbon dioxide is passed into water; (*b*) when it is passed into a clear solution of calcium hydroxide (limewater); (*c*) when it is poured over a flame.

6. Write the equation for the reaction that is used as a test for the presence of carbon dioxide.

7. Name three important commercial uses of carbon dioxide.

8. (*a*) Name the chemicals used in each of the common kinds of hand fire-extinguishers; (*b*) explain how each of these extinguishers operates.

9. Give (*a*) two physical properties that the two oxides of carbon have in common; (*b*) two ways in which they differ in chemical conduct.

10. Account for the formation of carbon monoxide (*a*) when hard coal is burned in a stove; (*b*) when a gas flame strikes a kettle of cold water.

11. Name (*a*) a property of carbon monoxide that makes the gas useful; (*b*) one that makes it dangerous.

12. Write the equation to represent the reaction that takes place when carbon monoxide burns.

13. What precautions should one take against being poisoned by carbon monoxide?

THOUGHT QUESTIONS

1. So far we have studied the following gases: (*a*) oxygen; (*b*) hydrogen; (*c*) carbon dioxide; (*d*) carbon monoxide. What properties have all these in common?

2. Describe what would take place if you introduced a burning splint into a bottle of each of the following gases: (*a*) oxygen; (*b*) hydrogen; (*c*) carbon dioxide; (*d*) carbon monoxide.

3. Why is it hard to liquefy carbon monoxide?

4. Why does not the druggist save money by using air in place of carbon dioxide in making soda water?

5. Complete the following table:

	CARBON DIOXIDE	CARBON MONOXIDE
(*a*) Color		
(*b*) Odor		
(*c*) Weight of 1 liter		
(*d*) Where found		
(*e*) Relation to combustion		
(*f*) Effect when breathed		
(*g*) Uses		

6. Both hydrogen and carbon monoxide burn with an almost colorless flame. How could you tell the difference between the two gases?

7. Carbon dioxide sometimes collects in deep wells and ravines. How could you test for its presence in such places?

8. The claim has been made for gas grates without chimney connections that they give no products of combustion. Can this be true?

9. How could you convert (*a*) carbon monoxide into carbon dioxide? (*b*) carbon dioxide into carbon monoxide?

10. Carbon dioxide contains 72.73 per cent of oxygen, and yet it is not a good oxidizing agent. Explain.

11. What are the sources of the carbon and the oxygen present in the carbon dioxide we exhale?

12. The diamond and graphite are both composed of carbon. How do we account for their wide difference in properties?

13. (*a*) Could you distinguish by appearance only between oxygen, carbon monoxide, and carbon dioxide? (*b*) If not, what simple test would enable you to distinguish between the three gases?

14. (*a*) How does destructive distillation differ from ordinary distillation? (*b*) Give an example of each.

15. Which of the following statements are true and which false? (*a*) Carbon dioxide is heavier than oxygen. (*b*) Carbon monoxide is a supporter of combustion. (*c*) "Dry ice," like ordinary ice, melts when exposed to the air. (*d*) Carbon dioxide is necessary for life.

OPTIONAL EXERCISES

1. Visit your fire department and find out all you can about the fire apparatus called "chemical," such as (*a*) the materials used in charging and the weight of each used; (*b*) how the apparatus is recharged after a fire; (*c*) the cost of the materials used in charging; (*d*) chemical reactions when the apparatus is in operation.

2. On a general average, a person exhales per minute about 8 liters of air (at body temperature) containing approximately 4 per cent by volume of carbon dioxide. Suppose there were 100 students in a schoolroom and there were no ventilation. How many liters of carbon dioxide at body temperature would be added to the air of the room each hour?

3. Show that the following results are in accord with two fundamental laws of chemical combination:

	By Analysis	Relative Weights
A sample of carbon monoxide contains	42.9% carbon	1
	57.1% oxygen	$1\frac{1}{3}$
A sample of carbon dioxide contains	27.3% carbon	1
	72.7% oxygen	$2\frac{2}{3}$

UNIT READINGS

Beery. *Stuff.* [Chapter III, "A Drink of Water," and Chapter VI, pp. 98–114, on coal, are simple and interesting.]

Clarke. *Marvels of Modern Chemistry.* [Chapter XII, on water, and Chapter XXIII, on carbon, are brief but worth reading.]

Faraday. *Chemical History of a Candle.* [A course of lectures delivered before a juvenile audience.]

Foster. *The Romance of Chemistry.* [Chapter V treats of oxygen and combustion; Chapter VII tells of hydrogen and water.]

French. *The Drama of Chemistry.* [Pages 23–32 give a brief but interesting account of Priestley, Cavendish, and Lavoisier.]

Jaffe. *Crucibles.* [Students will find the following chapters of great interest: Chapter IV, on Priestley; Chapter V, on Cavendish; Chapter VI, on Lavoisier.]

Leonard. *Crusaders of Chemistry.* [Chapter V tells of Boyle; Chapter VII, of Priestley; Chapter VIII, of Cavendish; and Chapter IX, of Lavoisier. The story of each is told in an interesting way, easy to understand.]

Mersereau. *Materials of Industry.* [Read pages 294–316, on coal.]

Price. "Dust Explosions in Industrial Plants," *Journal of Chemical Education,* Vol. III, pp. 1008–1017. [Good illustrations.]

Sadtler. *Chemistry of Familiar Things.* [Chapter VII gives some interesting facts about water.]

Weeks. *The Discovery of the Elements.* [Read of the discovery of the following: hydrogen (pp. 29–33); oxygen (pp. 35–48); carbon (pp. 3, 7–8).]

Worstell. *Journal of Chemical Education,* Vol. IX, p. 291. [An interesting article on ozone, most of which can be understood by students of elementary chemistry.]

The Science Leaflet. [No. 1 of Volumes VIII, IX, X, and XI contains information about water and its elements. No. II of the same volumes tells of carbon and its oxides.]

The World Book Encyclopedia. [Contains interesting articles on coal and diamonds.]

Unit Four. The Smallest Things in the World: What They Are and How They Act

NEARLY everyone likes a puzzle of some sort — a crossword puzzle, a detective story, a game of chess. The reason for this is that a puzzle draws on our imagination and our power of invention.

In this unit we shall be finding our way through some of the greatest and most interesting puzzles of science. What kind of things are the atoms and molecules of which all sorts of matter are made up? How big are they? Can we imagine pictures of them? What makes them combine with each other? If there are less than a hundred kinds of atoms, how can there be half a million different compounds? How do we find out the formulas of all these compounds?

You might be inclined to ask: What use is it to solve any of these puzzles? What have any of them to do with my pleasure in life? Well, if someone had not solved every one of them, and many more of the same kind, we should be living much as did the people in the time of Queen Elizabeth. We should have clothes to wear, and food to eat, and guns with which to hunt and fight, and horses and buggies to take us places. But we should not have many of the conveniences that make life today so rich. We should have no telegraphs or telephones, no railroads, no steamships, no automobiles, no radios, no movies, no modern medicine or surgery.

Is it not worth while, then, to call upon all our imagination and our inventive powers as we study how great minds have solved some of the most difficult problems of science?

CHAPTER XIII

Molecules and Atoms

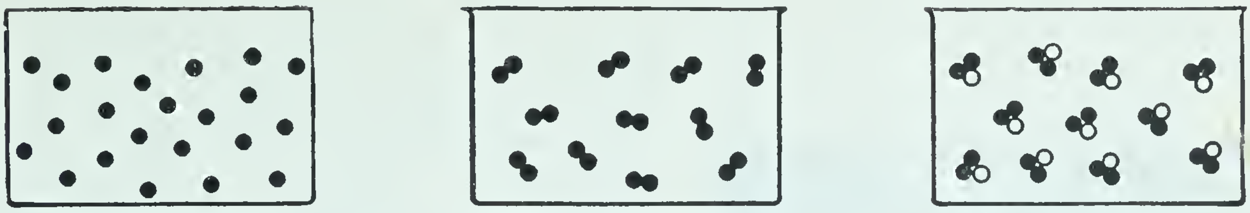
[Next to the Smallest Things in Chemistry]

Big things depend on very little ones. The industrial chemist spends his life making big things: tons of soap, or steel, or fertilizers, or paints. But he cannot start on this big scale. He begins by picturing to himself the way very small particles act on each other — particles so small that we can hardly imagine them. These minute particles are of two kinds, and are called *atoms* and *molecules*. We have already learned something about them (p. 33). In this chapter we shall have so much to say about them that we must be very sure we understand just what they are.

The atoms of an element. Everyone knows that if we take a piece of an elementary substance such as iron, we can grind or file it into smaller and smaller pieces until we have a mere powder of iron. But in a chemical action the smallest of these dust particles break up into much smaller ones, which then divide no further. These undividing particles of an *element* we call *atoms*. They are the smallest particle of an element that can be obtained.

The molecules of a compound. If we think of a *compound*, we see that its smallest particle must be made up of *at least* two atoms, one of one element and the other of a second element. If these two should part company, we should no longer have a specimen of the compound, but only the separate atoms of the elements that compose it. This least particle of a compound is called a *molecule* of the compound.

Molecules of elements. As already stated (p. 33), the atoms of some of the elements, such as oxygen and hydrogen, combine with each other to form molecules. For example, when oxygen is set free from a compound (as from water or potassium chlorate), we have every reason for thinking that it is set free as *atoms* of oxygen. But, as someone has said, "The atoms of many of the elements are sociable creatures" — they do not like to remain single. So each atom of oxygen gets a partner, and the two form a *molecule* of oxygen; or



Atoms of hydrogen *Molecules of hydrogen* *Molecules of water*

FIG. 115. The figure shows the relation between atoms of hydrogen, molecules of hydrogen, and molecules of water

The atoms of hydrogen are represented by black circles, and those of oxygen by white ones

they may prefer to unite instead with one or more atoms of some other element and so form a molecule of a compound (Fig. 115).

Most *metals* are unsociable, and their atoms do not unite with each other to form molecules; nor do the atoms of some rare gases, such as helium and argon.

The number of atoms in a molecule. The number of atoms in a molecule of an element varies with the element, but is nearly always small. As stated above, the atoms of the metals (and of some rare gases) form no molecules; or we may say that their atoms and molecules are identical. Most of the familiar elements, like oxygen, hydrogen, and nitrogen, have two atoms in their molecules. Ozone has three (so we represent its molecule as O_3), while phosphorus has four (P_4).

The molecules of the same compound always contain the same number of atoms, but the number varies according to the compound and is given in the formula. Thus the molecule of water has three atoms (H_2O), while that of sugar has forty-five atoms ($C_{12}H_{22}O_{11}$). How we get these formulas will be explained in due time.

Summary. We may now summarize the meaning of the terms *atom* and *molecule* as follows:

An atom is the smallest particle of an element that exists either alone or in combination with other atoms.

A molecule is the smallest particle of any element or compound that possesses all the properties of the element or compound. It is made up of two or more atoms of the same element (molecules of elements) or of different elements (molecules of compounds).

How large are the molecules? The way gases leak through very small holes, or pores, makes us very sure that the molecules composing these gases are extremely small. To help us realize how minute they really are, the great American chemist Langmuir (Fig. 116) has calculated that if the molecules in just one cubic inch of air were each to be suddenly changed into a grain of sea sand, the resulting sand would fill a trench three feet deep and one mile wide reaching from New York City to San Francisco.

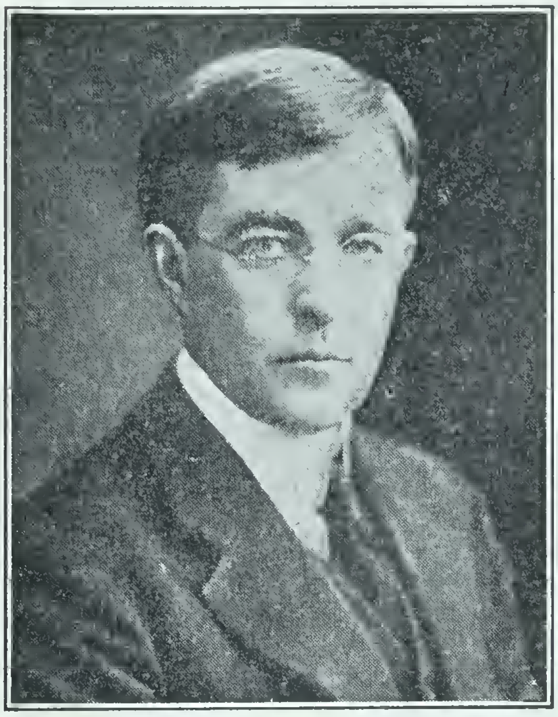


FIG. 116. I. Langmuir (1881–)
An eminent American chemist who has contributed much to our knowledge of atoms and molecules. In 1932 he received the Nobel prize, generally regarded as the greatest honor that can come to any scientist

Real and relative weights of atoms and molecules. Although the molecules are far too small to be seen by even the most powerful microscope, it is a wonderful fact that the chemist has found ways *to count the molecules in a given volume of a gas*. He can easily weigh this volume of the gas; and if he divides this weight by the number of molecules he has counted, he will have the *actual weight of the individual molecules.*

The trouble is that after he has made his calculation it is of little practical value to him; for the weights of atoms and molecules are so small — billionths of a milligram — that he is unable to make any use of them. It is as though a sugar merchant were to take the trouble to find out the weight of a single grain of sugar, whereas he always deals in pounds or tons.

Now we can measure the *relative* weights of the various kinds of molecules much more easily than their *actual* weights, and, as we shall see, we can make many uses of these relative weights. Before explaining how this is done, it is important to have clearly in mind just what we mean by *relative* weights.

Meaning of relative values. We are constantly using *relative* values instead of *actual* ones without thinking about it. Our forefathers picked out a stick for measuring and called it a *foot*, dividing it into twelfths called *inches* and multiplying it by three to make a *yard*. The inch and the yard are relative to the foot, and the latter is wholly arbitrary. It might have been any other convenient length, and we should then have had longer or shorter inches and yards; but they would still have had the same ratio to each other.

Standard for atomic and molecular weights. Since we have decided to use relative rather than absolute weights for atoms and molecules, let us follow the example of our forefathers and pick out an arbitrary standard for this purpose — a chemical foot, as it were. Now oxygen combines with nearly all the elements; so it is most convenient to take the oxygen atom as standard and to give it the value 16. This value is arbitrary, like the length of the original foot-stick. But since there are 2 atoms in the oxygen molecule, we may equally well choose the oxygen molecule as our standard and give it the value 32. Evidently these two standards amount to the same thing.

Why choose the weight 16 for the oxygen atom? We want to give our standard a round number; and if we make this number less than 16, some kinds of atoms will have weights less than 1. We want to avoid this. With the value 16 for the oxygen atom, the lightest of all atoms (hydrogen) will have a value just above 1, or exactly 1.0081. We can now understand the following important definitions:

The atomic weight of an element is the relative weight of its atom compared with the weight of the oxygen atom, fixed at 16.

The molecular weight of a compound (or of such elements as form molecules) is the relative weight of its molecule compared with the weight of the oxygen molecule, fixed at 32.

Table of atomic weights. Later on we shall describe the way in which chemists have succeeded in measuring both atomic weights and molecular weights. Meanwhile a complete list of atomic weights will be found on the inside back cover page of this book.

HOW WE CAME TO BELIEVE IN ATOMS

The atomic theory. From the time of the early Greeks, four centuries before the beginning of the Christian Era, some philosophers argued that matter is made up of atoms, or indivisible particles, while others denied that this is so. But there were no proofs either way; so these views were merely speculation (p. 4).

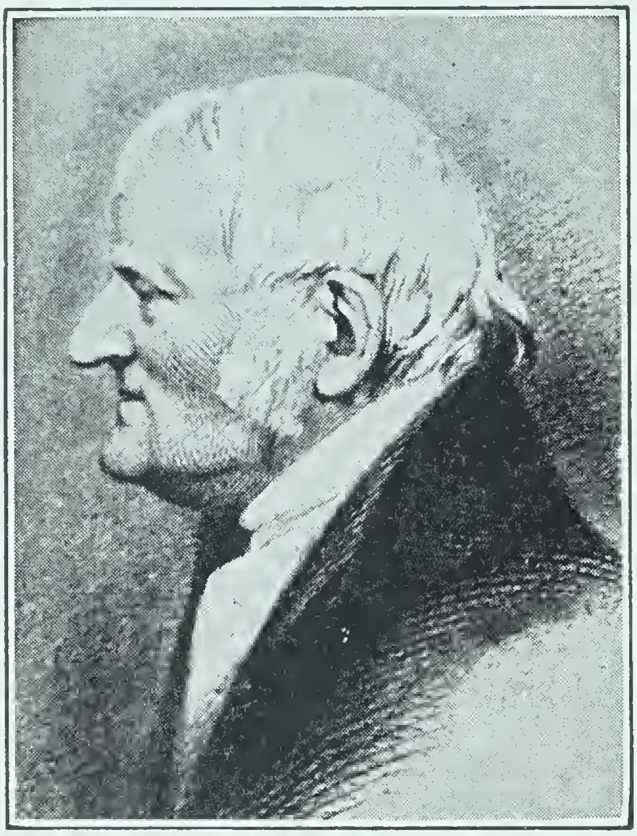


Fig. 117. John Dalton (1766–1844)

A famous English teacher and scientist. He made many discoveries, but his greatest contribution to science was his development of the atomic theory. (Courtesy of Dr. Harold Hibbert, McGill University)

More than a century ago (1808) the Englishman John Dalton (Fig. 117) saw that the way gases act, and especially **the law of definite composition** (p. 130), gave proofs for the first time that matter *acts* as though it were made up of atoms. Chemists eagerly sought for other proofs, and have found so many of them that there is no longer any doubt about atoms. We are certain that all forms of matter are made up of atoms and of their combinations in molecules.

What atoms are like. Since we cannot see atoms, we can only guess what they are like from the way they act. Dalton thought of them as absolutely indivisible; for he is quoted as saying, "Thou knowest that no man can split an atom." Today we have very good reason for a different view. We believe that an atom is made up of different parts, or units, and that it resembles our solar system in that it has a very heavy center, or nucleus, corresponding to the sun, with much lighter satellites, like planets, spaced around the nucleus. This picture will be described in detail in the next chapter.

The scientific method for finding truth. We hear much today about the *scientific method* for getting at the truth about things. What do we mean by this? We can get a clear idea by studying the development of the atomic theory.

Steps in the development of the atomic theory. (1) The Greek *speculations* were of little value because they were based on *no known facts.* The first real step was taken when (2) men began to *experiment* on how gases act under varying pressure, and especially when (3) they had *proved* that a given compound has a perfectly definite composition. (4) Men then wanted to know the *cause* of this definite composition, and it was John Dalton who clearly *imagined* this cause. He saw that if matter is made up of atoms, each kind having its own definite weight, the law of definite composition would be explained at once.

For example, if two kinds of atoms, *A* and *B*, have the weights 5 and 10, and it is their habit to combine one atom of *A* with one of *B*, then each molecule of the compound formed will be made up of the two elements in the ratio by weight of 5 : 10, or 1 : 2. Every sample of the compound, made up of such molecules, will have this same ratio of 1 : 2 by weight in composition.

(5) Dalton also *predicted* that if, in a different compound, 2 atoms of *A* were to combine with 1 atom of *B*, then the ratio by weight in any molecule would be 10 : 10, or 1 : 1. And this would be true of any number of molecules or any weight of the compound. He quickly *proved* this true and so gave the *reason* for the law of multiple proportion (p. 134).

Steps in the scientific method. So the steps in the scientific method are these:

1. Suppose you have found some facts or laws that are so interesting or unexpected that they demand an *explanation.*

2. *Imagine* an explanation which, if it were true, would fit the facts in the case. This is called *making a theory.*

3. Invent many experiments to test whether the explanation or theory fits all the facts in the case.

4. If the theory is found to fit the facts, accept it as the truth until some other facts come to light that do not fit. A new theory must then be imagined, to include the new facts.

5. By experiment, follow up everything suggested by the theory in the search for new knowledge.

CHAPTER SUMMARY IN QUESTION FORM

1. (*a*) State clearly what we mean by the terms *molecules* and *atoms.* (*b*) Give some idea of the size of molecules.

2. Distinguish between (*a*) the molecules of a compound and (*b*) the molecules of an element.

3. Name (*a*) some elements whose atoms combine to form molecules, and (*b*) others whose atoms do not.

4. (*a*) Explain what is meant by the term *relative weights.* (*b*) Why does the chemist deal with relative weights of atoms and molecules rather than with actual weights?

5. (*a*) For the relative weights of atoms and molecules what standard has been selected? (*b*) What value is given this standard? (*c*) Why not select the element of lightest atomic weight (hydrogen) as the standard and give it the value 1?

6. What is meant by (*a*) *atomic weight* and (*b*) *mclecular weight*?

7. (*a*) Who formulated the atomic theory of matter? (*b*) Is the statement "All matter is made up of atoms" any longer a theory, or has it become an established fact?

8. (*a*) Explain what is meant by the term *scientific method* and (*b*) give the different steps in this method.

THOUGHT QUESTIONS

Match the name of each person in column *A* with the number (or numbers) showing the contribution made by each as given in column *B*. (Do not write in the book.)

A	*B*
Perkin	1. Made diamonds in the laboratory.
Stahl	2. Discovered hydrogen.
Hall	3. Advanced the phlogiston theory.
Charles	4. Made the first aniline dye.
Cavendish	5. Showed how the volume of a gas varies with pressure.
Boyle	6. Gave the true explanation of combustion.
Moissan	7. Proved that water is a compound of oxygen and hydrogen.
Priestley	8. Showed how the volume of a gas varies with the temperature.
Lavoisier	9. Advanced the atomic theory.
Dalton	10. Found a cheap way of producing aluminum.
	11. Discovered oxygen.

OPTIONAL EXERCISE

In a certain school 160 pupils are studying English; 120, history; 100, science; 40, Latin; 10, Spanish. Find the relative number of pupils in each of these subjects in terms of the number studying Spanish. Show how this illustrates atomic weights.

CHAPTER XIV

The Structure of the Atom

[Each Atom a Tiny Solar System]

What is an atom really like? We may imagine that John Dalton, and those who came after him for nearly a century, thought of an atom much as a child might think of a watch. A watch is a round, flat object, of definite size and weight, that does just one thing — tells time. So Dalton's atom had size and weight and did one thing: it combined with other atoms. That was about all that was known of it.

Now let us suppose that one day someone let a watch fall so that it broke open. Out came wheels and spring and screws; so it was clear that the watch was a mechanism that had structure. This is much like what the physicists have been doing to the atoms for the past thirty years. They have been smashing the atoms and trying to find out what came out of them.

But the problem is a much more difficult one than trying to solve the mysteries of the watch. For not only are the parts of the atom so minute that they are hard to detect, but when they are detected it is still more difficult to find out how they were fitted together to form the atom. A good beginning has been made, however, and the knowledge of today is of great help to the chemist. The experiments that have led to our present knowledge are very hard to understand and do not belong in an elementary text; but we may describe the more important results that have been reached.

What is electricity? In the time of Benjamin Franklin (Fig. 118) most philosophers thought there were two *kinds* of electricity (or electrical fluids, as they called them). Bodies containing the same kind of electricity repelled each other; bodies containing different electricities attracted each other. Franklin disagreed with this and thought there was but one kind. If a body had too much of it he said it had a *positive* (+) charge; if not enough, it had a *negative* (–) charge. If it had its natural amount, it showed no electrical properties. The modern physicist has other ideas.

Two kinds of electrical units or particles: the proton and the electron. The physicist has succeeded in getting two kinds of electrical *particles* from the atom. Each has a definite weight and is just the same, no matter from what atom it comes. As a result of this discovery we now believe that electricity is made up of unit charges, or particles, or electrical "atoms," just as we feel sure that matter is made up of chemical atoms.

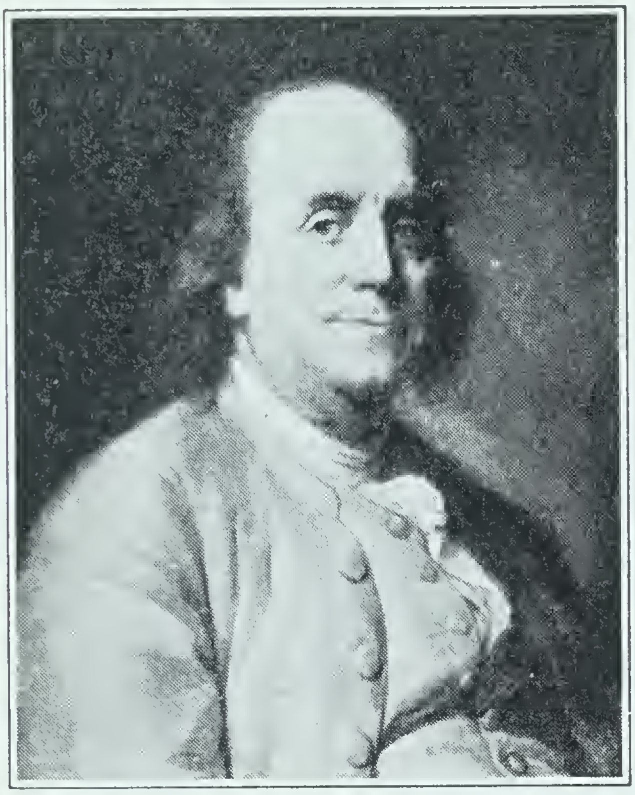


FIG. 118. Benjamin Franklin (1706–1790)

An eminent statesman and one of the greatest scholars of his time. Among many other things, he was interested in electricity. He showed that lightning is just a huge electric spark, and invented lightning rods to protect buildings

The particle of what we today call *positive* (+) electricity is known as a *proton.* In weight it is a trifle lighter than the hydrogen atom; to be exact, it is $\frac{1844}{1845}$ of that weight. The particle of *negative* (−) electricity is called an *electron.* It is very light, being only $\frac{1}{1845}$ of the weight of the hydrogen atom. Although these two kinds of electrical particles differ so greatly in weight, *their electrical charges are equal,* but opposite in electrical properties.

The neutron. A third kind of particle, called a *neutron,* has also been obtained from the atoms of various elements. As its name suggests, it is neutral; that is, it has no electrical properties. Its weight is about the same as that of the proton, so that for all practical purposes we may consider the weights of the neutron and proton as identical.

The positron. A fourth kind of particle has been found in the wreckage of some atoms, and to this the name *positron* has been assigned. Not much is known about it or how it fits into the structure of the atom; indeed, it may not be present as such in the atom, but may be formed when the atom is knocked to pieces. It is positive in charge, as its name suggests, and has about the same mass as an electron. Possibly a proton is a combination of a neutron and a positron.

The parts of an atom. The following table gives the names of the four kinds of particles found in the wreckage of atoms, as well as their electrical sign and their mass.

NAME	ELECTRICAL SIGN	WEIGHT (MASS)
Proton . .	Positive by 1 unit	Nearly that of the hydrogen atom, namely, 1
Electron . .	Negative by 1 unit	$\frac{1}{1845}$ of the hydrogen atom
Neutron . .	Neutral	About that of the proton
Positron . .	Positive by 1 unit	About that of the electron

Since at the present time so little is known of the positron, we shall not mention it further in the study of the structure of the atom.

The number of protons and that of electrons in an atom are equal. It is well known that equal quantities of positive and negative electricity neutralize each other. But equal quantities of opposite electricity mean equal numbers of protons and electrons. Now *the atoms of the elements are neutral* under all ordinary conditions; so each kind of atom must have in it equal numbers of protons and electrons. So we can start with these facts to build up a picture or theory of atomic structure.

How protons, electrons, and neutrons are arranged in the atom. The particles which make up the atom are not thrown together in a jumble, but the atom of each element has its own wonderful structure. In all atoms there are two parts: (1) the nucleus, or central body, and (2) the electrons at a distance from the nucleus.

The nucleus. All the protons and neutrons present in any atom are lodged in the nucleus, which is very small and dense. All the electrons are outside of the nucleus. Since the atom as a whole is neutral, there must be just as many protons in the nucleus as there are electrons outside of it. For our purposes we may regard the *weight* of the atom as equal to the sum of the weights of the protons and neutrons present in its nucleus; for the electrons are so light that their weights may be disregarded.

The electrons. Relative to their sizes, the electrons are far distant from the nucleus and are spaced out at very definite distances. We usually think of them as revolving about the central nucleus much as the nine planets revolve about our sun. Indeed, relative to their size, the distant electrons are about as far from the nucleus as the distant planets are from the sun. So an atom has *relatively* as much empty space in it as does our solar system (Fig. 119).

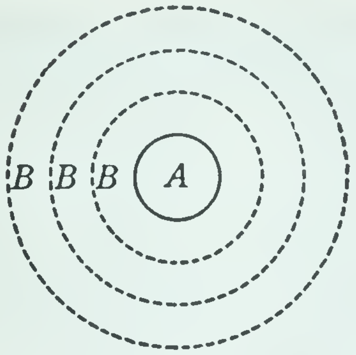


Fig. 119. General model of an atom

The protons and neutrons make up the nucleus *A*. The electrons revolve about the nucleus in a series of orbits *B*, *B*, *B*

The atomic number. One of the important discoveries in connection with the study of the structure of the atom has been the finding of a way to measure the electrical charge of the nucleus of the atom. We call this electrical charge the *atomic number of the element*, often abbreviated to A.N. Since the nucleus contains all the protons and none of the electrons, and since each proton carries a unit charge, it follows that *the atomic number of any element must be the same as the number of protons in the atom of the element.*

The setting up of a model of an atom. We now have the information required to set up a sort of model of an atom. To do this we must first know the atomic number of the element whose atom we wish to represent, as well as its atomic weight. Both these values for each of the elements have been measured, and are given in the table on the inside of the back cover of the text.

1. ***The make-up of the nucleus.*** The nucleus is made up of protons and neutrons. The number of protons present in the nucleus of the atom of any element is the same as the atomic number of the element. To find the number of neutrons present we have only to subtract the sum of the weights of all the protons present from the atomic weight of the element (using the nearest whole number); for the weight of the atom is the sum of the weights of all the protons and neutrons present. In making this calculation, it is accurate enough to count each proton and each neutron as hav-

ing a weight of 1, whereas the weight of the electron is so small that it may be disregarded.

2. ***The position of the electrons.*** We know that the number of electrons is the same as the number of protons. But what about their position? We know that they are outside the nucleus and undoubtedly are in motion, but we are not sure about their exact position and motion. Experiments seem to show that they revolve in orbits about the nucleus; and that not more than 2 revolve in the orbit nearest the nucleus, not more than 8 in the second orbit, and, in the case of elements with an atomic number not above 25, not more than 8 in the third. Sometimes we say that they revolve in *concentric shells* about the nucleus rather than in orbits. It makes little difference which of these two terms we use; so we shall say *orbit*, since in our diagrams it is simpler to represent the atoms as revolving in orbits.

General model of the atoms. Keeping all these facts in mind, it is a simple matter to draw diagrams showing the structure we give to the atoms at the present time. Let us begin with the atoms of the first ten elements in the order of increasing atomic numbers. We will represent the nucleus by a small inner circle, the electrons by black dots (or balls), and the orbits in which the electrons revolve by circles surrounding the nucleus. Within the nucleus are shown the number of protons (*p*) and neutrons (*n*) necessary to make up the atomic weight. Below each diagram is given the atomic number (A.N.).

The model of the first ten elements. Since hydrogen has an atomic number of 1, its atom must contain 1 proton and 1 electron, as shown in Fig. 120. The weight of the proton is identical (or nearly so) with the atomic weight of the element; so no neutrons can be present. Helium has an atomic number of 2; so its atom must contain 2 protons and 2 electrons. But the atomic weight of helium is 4, while the 2 protons present weigh only 2; so there must be 2 neutrons in the nucleus along with the 2 protons, as shown in Fig. 121. The lithium atom (atomic number, 3) contains 3 protons and 3 electrons. But the atomic weight of lithium is 7; so the nucleus must contain 4 neutrons in addition to the

3 protons, in order to give the correct atomic weight. Since not more than 2 electrons revolve in the inner orbit, the

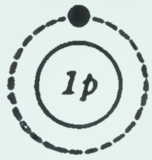

Hydrogen
1p
A.N. 1

Fig. 120

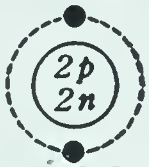

Helium
2p
2n
A.N. 2

Fig. 121

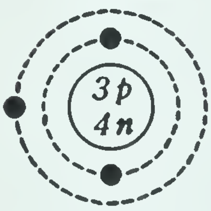

Lithium
3p
4n
A.N. 3

Fig. 122

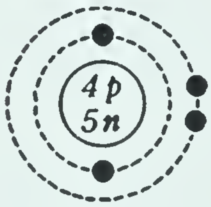

Beryllium
4p
5n
A.N. 4

Fig. 123

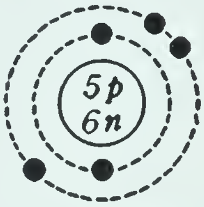

Boron
5p
6n
A.N. 5

Fig. 124

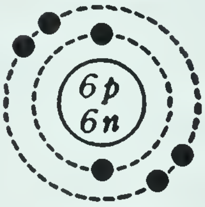

Carbon
6p
6n
A.N. 6

Fig. 125

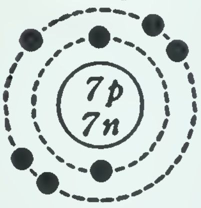

Nitrogen
7p
7n
A.N. 7

Fig. 126

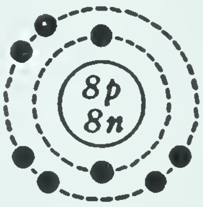

Oxygen
8p
8n
A.N. 8

Fig. 127

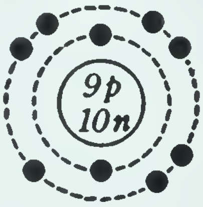

Fluorine
9p
10n
A.N. 9

Fig. 128

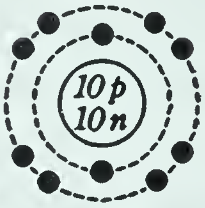

Neon
10p
10n
A.N. 10

Fig. 129

third electron revolves in the second orbit, as shown in Fig. 122. In a similar way the student can easily account for the structure of the remaining seven elements, as shown in Figs. 123 to 129.

The model of atoms with more than ten electrons. If more than 10 electrons are present, the additional ones, up

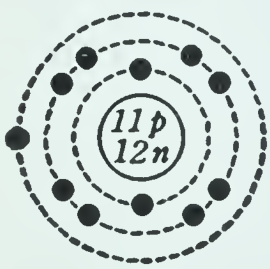

Sodium
11p
12n
A.N. 11

Fig. 130

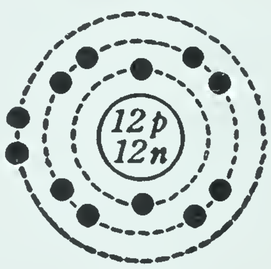

Magnesium
12p
12n
A.N. 12

Fig. 131

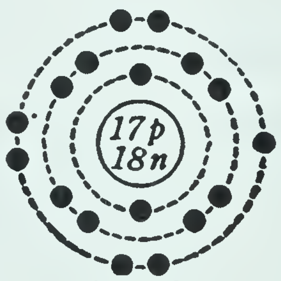

Chlorine
17p
18n
A.N. 17

Fig. 132

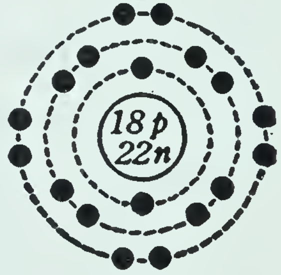

Argon
18p
22n
A.N. 18

Fig. 133

to 8, revolve in a third orbit. The structure of four such atoms is shown in Figs. 130–133. If the number of electrons exceeds 18 (2 in the first orbit, 8 in the second, and 8 in the third), the extra ones revolve in additional orbits. Atoms containing from 19 to 25 electrons (inclusive) have 2 in the first orbit, 8 in the second, 8 in the third, and the remaining ones in a fourth orbit. In atoms containing more than 25 electrons the arrangement is less simple. Students interested in the subject will find a complete list of the arrangement of the electrons in all the known elements in *The Science Leaflet*, Vol. 10 (1936), pp. 20–22.

Summary of our knowledge about the structure of the atom. Because of the importance of the subject, let us now sum up the main facts about the structure of the atom.

1. Atoms are made up of three different units called *protons*, *neutrons*, and *electrons*.

2. The protons and neutrons have each about the same weight as the hydrogen atom, that is, approximately 1. The electrons have little weight — only about $\frac{1}{1845}$ that of the hydrogen atom.

3. Each proton carries a unit positive electrical charge; each electron, a unit negative charge. The neutron carries no charge.

4. Since atoms are electrically neutral, each atom must contain the same number of protons and electrons.

5. The units that compose any atom have a definite arrangement. The protons and neutrons form a central core, or *nucleus*, while the electrons revolve about the nucleus in definite orbits, 2 electrons in the orbit next the nucleus, not more than 8 in the second orbit, and (except for atoms containing more than 25 electrons), not more than 8 in the third.

6. The atomic weight of any atom is approximately equal to the sum of the weights of all its protons and neutrons. The electrons are so light that we do not need to count their weight.

7. The nucleus always carries a positive charge equal to the sum of the charges of its protons. This positive charge of the nucleus of the atom is called the *atomic number* of the element. It is equal to the number of protons in the atom, as well as the number of electrons.

Summary of the way to draw a picture of an atom. 1. Note the atomic number of the element whose atom we wish to picture. This is the same as the number of protons as well as of electrons present.

2. Subtract the sum of the weights of the protons from the atomic weight of the element. The difference equals the number of neutrons present.

3. Arrange all the protons and neutrons in the nucleus of the atom, and the electrons in orbits about the nucleus — 2 in the innermost orbit, not more than 8 in the second orbit, and (except for atoms containing more than 25 electrons) not more than 8 in the third.

CHAPTER SUMMARY IN QUESTION FORM

1. Contrast Dalton's idea of an atom with that held at the present time.

2. (*a*) Name the different particles, or units, that go to make up the structure of the atom. (*b*) Give the approximate weight and (*c*) the electrical charge of each.

3. (*a*) Where are the protons in any atom located? (*b*) Where are the neutrons? (*c*) Where are the electrons?

4. (*a*) Is the charge on the nucleus positive or negative? (*b*) How does the charge on the nucleus compare with the number of protons present? (*c*) What name do we give to the electrical charge on the nucleus of the atom of any element?

5. How does the number of electrons in any atom compare with the number of protons?

6. Give the number of electrons and their location in the atoms of elements having the following atomic numbers: (*a*) 1; (*b*) 5; (*c*) 8; (*d*) 12; (*e*) 15; (*f*) 18; (*g*) 20.

7. Since every atom contains both positive and negative charges of electricity, how do we account for the fact that all the atoms are electrically neutral?

8. What information must we have about an atom in order to construct a model of the atom? (*b*) Having this information, how can we find the number of protons, neutrons, and electrons in the atom?

9. Illustrate how to plan the model of an atom, using as examples an atom of each of the following elements: (*a*) hydrogen; (*b*) helium; (*c*) lithium; (*d*) oxygen; (*e*) carbon; (*f*) neon.

THOUGHT QUESTIONS

1. In the table on the inside of the back cover of the text find the atomic number and the atomic weight of each of the following elements, and draw a diagram showing the structure of the atom of each: (*a*) aluminum; (*b*) phosphorus; (*c*) potassium; (*d*) manganese.

2. The electrons in the atom of iron revolve in four orbits: 2 in the first orbit, 8 in the second, 14 in the third, and the remaining ones in the fourth. Draw a diagram showing the structure of the iron atom.

3. What part of an atom weighs the most?

OPTIONAL EXERCISE

Using a large wooden bead for the nucleus, small beads for each of the electrons, and wire for the orbits of the electrons, construct models of the atoms of one or more different elements. (These beads can be purchased at any ten-cent store.)

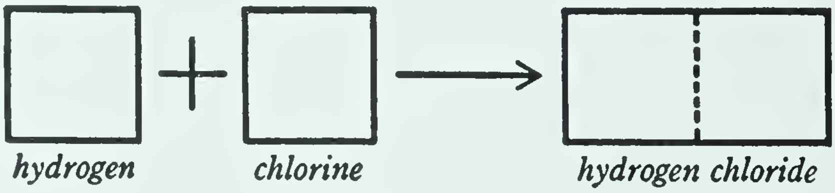
CHAPTER XV

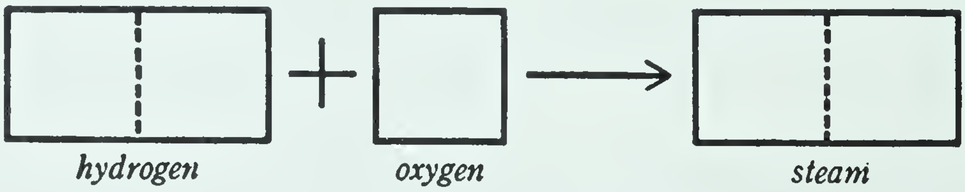
How We Find Molecular and Atomic Weights

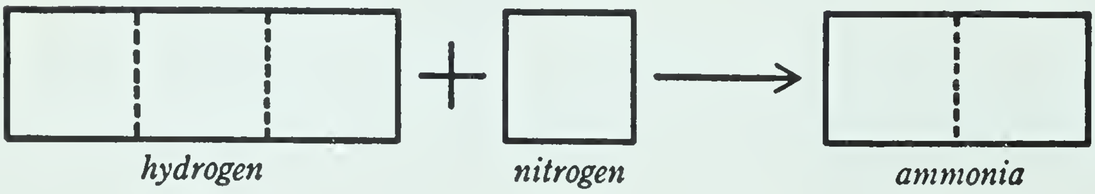
[A Problem It Took Chemists Many Years to Solve]

The problem. We have seen that the actual weights of atoms and molecules are far too small to be of any service to us; so we use their *relative* weights. How, then, can we find these relative weights and express them in numbers of convenient size for use? Two important laws show us how.

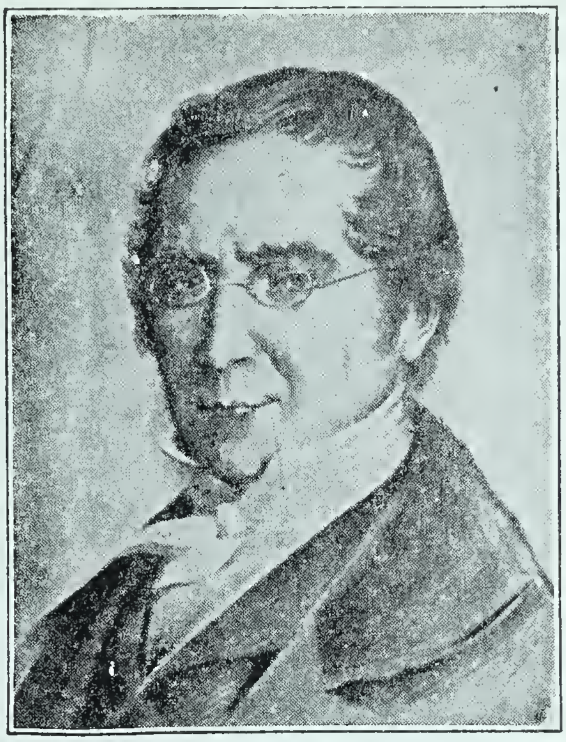
The law of combining volumes. In studying the composition of water (p. 128) we found that 2 volumes of hydrogen combine with 1 volume of oxygen to form 2 volumes of steam, the gases and vapor, of course, being measured under the same conditions of temperature and pressure. It is a surprising fact that these three volumes can all be stated in *whole numbers*, and we wonder if this just happens to be true in this special case or whether it is a general rule. Experiments show that when *any* two gases combine, their relative volumes, as well as the volume of the product formed (if it is a gas or vapor), can always be stated in small whole numbers. Examples of this fact are shown as follows:







One volume of hydrogen unites with one volume of chlorine; two volumes of hydrogen with one of oxygen; three of hydrogen with one of nitrogen.



A distinguished French scientist. He showed the variation of the volume of a gas with its temperature, as did also Charles and Dalton at about the same time; determined accurately the ratio by volume in which hydrogen combines with oxygen, as well as the combining ratio of many other pairs of gases; and so formulated the law which bears his name. He made many improvements in analytical processes. He was one of the great teachers of his generation and held a number of public offices, including membership in the House of Peers

FIG. 134. Joseph Louis Gay-Lussac (1778–1850)

This surprising regularity was first noticed in 1808 by the French chemist Gay-Lussac (Fig. 134). The following statement of it is called *Gay-Lussac's law of volumes.*

GAY-LUSSAC'S *Law: When two gases combine chemically, there is always a ratio of small whole numbers between the volumes that combine, as well as between the volume of either of them and that of the product (provided it is a gas).*

Avogadro's law. The Italian scholar Avogadro (Fig. 135), born in the year of our Declaration of Independence, was greatly impressed by the simple relations summed up in the law of volumes. Why should this law be true? To answer his own question, he made a very happy guess which we now call *Avogadro's law.* This may be stated as follows:

AVOGADRO'S *Law: Equal volumes of all gases, measured under the same conditions of temperature and pressure, contain the same number of molecules.*

Avogadro could not prove his guess to be true; but we now know it to be a statement of a general fact, and we call it a law. It has been of the greatest service to chemists; for it makes it possible for them to measure the relative weights of molecules, as we shall now see.

Relative molecular weights. While it is not so easy to weigh gases as it is liquids or solids, it is possible to weigh them with great accuracy; and we find that under standard conditions of temperature and pressure

1 liter of oxygen weighs 1.429 g
1 liter of hydrogen weighs 0.08987 g
1 liter of nitrogen weighs 1.2506 g

Now these three weights are the weights of equal volumes of the three gases, and, by Avogadro's law, there is the same number of molecules in each of the three liters. So it is clear that these three numbers, 1.429, 0.08987, and 1.2506, *state the relative weights of the three kinds of molecules*, just as from the *actual* weights of 100 pennies, 100 nickels, and 100 dimes we can get the *relative* weights of the penny, the nickel, and the dime.

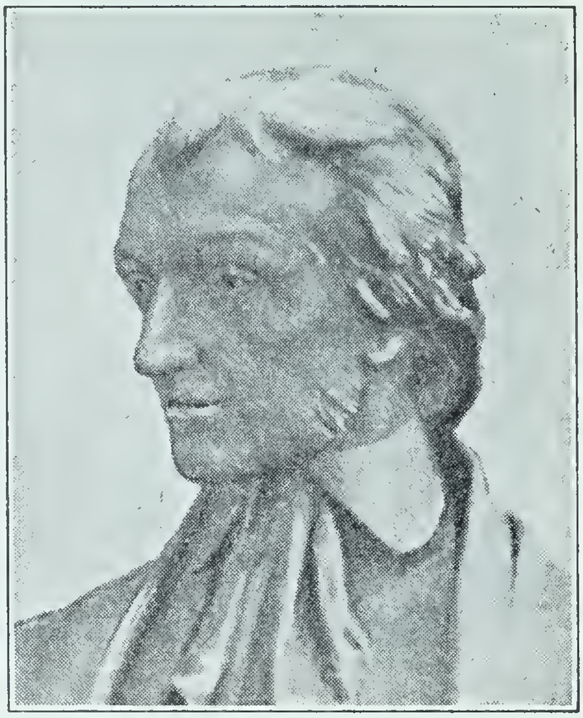


FIG. 135. Amedeo Avogadro (1776–1856)

Professor at the University of Turin, in Italy. Renowned for formulating the fundamental principle of modern chemistry known as Avogadro's law. (From a photograph of a statue erected to his memory in Turin)

Evidently we may argue the same way about all other gases; so we may conclude that *the relative weights of 1 liter of various gases give us their relative molecular weights.*

Standard for molecular weights. All we now need to do is to decide upon some suitable standard for molecular weights and give it a convenient value, just as we picked out the dollar as a standard in coins and gave it the value 100. We have already seen (p. 165) that chemists have selected the oxygen molecule as the standard and have assigned to it the number 32 as its weight. The reasons for selecting this standard have already been given, and it is not necessary to repeat them here.

Molecular weights from the weight of 22.4 liters. Having agreed upon the value 32 for our standard oxygen molecule, let us next calculate the volume occupied by 32 g of oxygen gas. Since 1 liter of oxygen weighs 1.429 g, the volume occupied by 32 g will be $\frac{32}{1.429}$, or 22.4 liters. If we make a vessel that has a volume of exactly 22.4 liters, and fill it with oxygen, it will hold the standard molecular weight (measured in grams), namely 32 g (if the vessel is a cube, each edge will be 28.2 cm long).

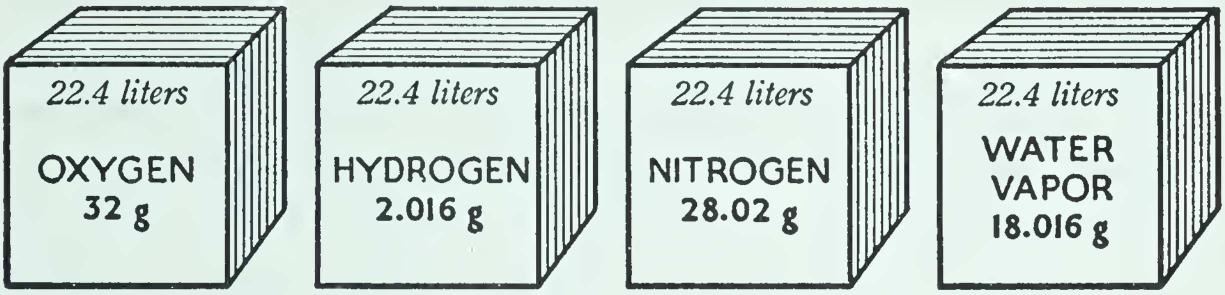


FIG. 136. The weight of 22.4 liters of various gases

If we now replace the oxygen in the vessel with nitrogen, the same number of molecules will be present as when it was filled with oxygen (Avogadro's law), and experiments show that the weight of the 22.4 liters of nitrogen is 28.02 g. But these two numbers, 32 (the weight of 22.4 liters of oxygen) and 28.02 (the weight of 22.4 liters of nitrogen), must be the relative weights of an equal number of molecules. It follows, then, that the nitrogen molecule weighs 28.02 compared with the oxygen molecule (32).

By the same reasoning, the weight in grams of 22.4 liters of *any* gas or vapor will give its molecular weight compared with oxygen (taken as 32) (Fig. 136). *The volume 22.4 liters is called the gram-molecular volume.*

In numbers the molecular weight of any gaseous element or compound is the same as the weight in grams of 22.4 liters of the gas.

It should be added that the molecular weights got in this way are not *exactly* correct (though very nearly so), because no gas exactly obeys the laws of gases. But they are accurate enough for our purposes.

Molecular weights of solids and liquids. While we have this simple way of finding the molecular weights of gases and vapors, solids and pure liquids give us much more trouble. Indeed, we have already seen (p. 49) that crystallized solids have no true molecular weights, their atoms (or groups of atoms) being arranged in regular space forms. Methods for determining the molecular weights of pure liquids give us very uncertain results and need not be described.

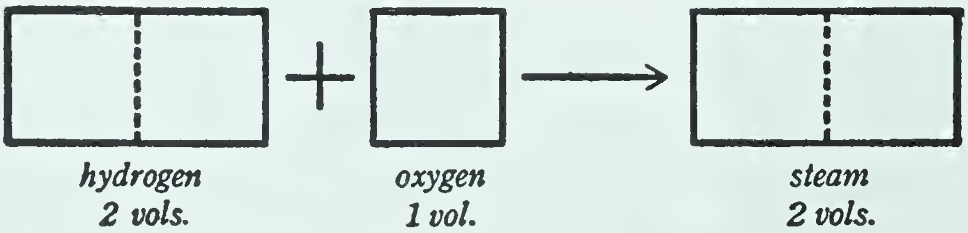
Molecular weight of a nonelectrolyte in solution. For gases Avogadro's law is of the greatest help to us because it gives us a way to be sure we are dealing with *an equal number of molecules* in equal volumes of all gases. In 1883 the French scientist Raoult found a law that gives us this same information about equal numbers of *dissolved* molecules. This law holds good for nonelectrolytes only, and in very dilute solutions. It may be stated thus:

Law of RAOULT: *Equal numbers of molecules of any nonelectrolytes lower the freezing point of a given volume of a given solvent to the same extent.*

How Raoult's law may be used. Raoult found that the molecular weight in grams of any nonelectrolyte will lower the freezing point of 1 liter of water 1.87°. So if we take 1 liter of water and add (say) sugar until the water just begins to freeze at – 1.87°, we shall have added the molecular weight (in grams) of sugar. It will take 342 g, and so 342 is the molecular weight of sugar.

How many atoms are there in a molecule of oxygen? We have been assuming that the oxygen molecule is made up of two atoms (p. 33); but how do we know this to be true? The reasoning is as follows

We have found by experiment that when hydrogen and oxygen combine to form steam, the volume relations are as shown in the following diagram:



Now let us suppose that the 1 volume of oxygen taking part in the reaction contains 100 molecules. Then the two volumes of steam formed must contain 200 molecules of steam, in accordance with Avogadro's law. But each of these 200 molecules of steam must have at least 1 atom of oxygen, or 200 atoms in all. But these 200 atoms of oxygen came from the 100 molecules of oxygen; so each molecule of oxygen must have at least 2 atoms. Similar reasoning from other reactions shows that the molecule of hydrogen must likewise have at least 2 atoms.

The above reasoning simply proves that there must be *at least* 2 atoms in each of the oxygen and hydrogen molecules. There might be more, but there is no evidence that points that way. Indeed, all evidence leads to the conclusion that there are only 2 atoms present in each of these molecules; so we assume this to be correct.

The atomic weights of hydrogen and oxygen. Since we have adopted 32 as the molecular weight of oxygen, and since the molecule contains 2 atoms, it follows that the atomic weight of oxygen must be 16. With this standard the atomic weight of hydrogen must be approximately 1 (to be exact, 1.0081), and those of all other elements are greater than unity.

Relative atomic weights. Having found methods for measuring the relative molecular weights, we should next like to find ways for measuring the atomic weights not only of oxygen and hydrogen but of the atoms of all the different elements. This has proved to be a harder problem. But since we are able to measure the relative weights of molecules *made up of atoms*, ways have been found to get the atomic weights from the molecular weights. The methods used are rather confusing to the beginner in chemistry. We shall simply ask him to accept the fact that the relative atomic weights of all the elements have been measured with accuracy. A list of these weights will be found on the inside of the back cover. We do not have to know how they were obtained in order to use them intelligently.

Importance of atomic and molecular weights. The chemist depends upon his knowledge of atomic and molecular weights just as much as the carpenter depends on his foot rule, or the surveyor on his level. All his calculations are based on them, and we must understand their meaning and how to use them if we are to make any progress in our study of chemistry.

Fractional atomic weights. It will not escape the notice of the thoughtful student that, since the weight of the proton and of the neutron is 1, while that of the electron is practically negligible, the atomic weights should all be multiples of 1; that is, whole numbers or very nearly so. When we look at the table of the atomic weights of the elements as given on the inside of the back cover of the book, we find this is not true; for many of the elements have fractional atomic weights. The reason for this will be given later.

CHAPTER SUMMARY IN QUESTION FORM

1. Define the terms (*a*) *atomic weight* and (*b*) *molecular weight.* (*c*) Why do we use relative weights rather than actual weights?

2. (*a*) State the law of combining volumes. (*b*) Who first observed the facts stated in this law? (*c*) Give three illustrations of the law.

3. (*a*) Who was Avogadro and (*b*) when did he live? (*c*) State the law that now bears his name.

4. (*a*) Show how Avogadro's law enables us to determine the relative molecular weights of gases. (*b*) Illustrate by determining the relative molecular weights of oxygen, hydrogen, and nitrogen.

5. (*a*) What is our standard for molecular weights? (*b*) Why was this particular standard chosen?

6. Calculate the volume of a vessel that will just hold the standard molecular weight, measured in grams, of oxygen.

7. To find the molecular weight of any gas, we have only to find the weight in grams of how many liters of the gas?

8. What name is given to the volume 22.4 liters of a gas?

9. (*a*) How many atoms are there in a molecule of oxygen? (*b*) Give proof of your answer.

10. How can we find the atomic weights of gaseous elements?

11. How can we find the molecular weight of a nonelectrolyte dissolved in water?

THOUGHT QUESTIONS

1. Is it possible to have (*a*) an atom of an element? (*b*) a molecule of an element? (*c*) an atom of a compound? (*d*) a molecule of a compound?

2. Why do we believe that all the molecules of the same compound are alike?

3. What happens to the molecules of water (*a*) when the water is changed into steam? (*b*) when it undergoes electrolysis?

4. Knowing the weight of 1 liter of each of the following gases (Appendix E), calculate the molecular weight of each: (*a*) carbon dioxide; (*b*) carbon monoxide; (*c*) hydrogen sulfide.

5. Show that the fact that 2 volumes of hydrogen combine with 1 volume of oxygen to form 2 volumes of steam is in accord with Avogadro's law.

6. 3 volumes of oxygen will give 2 volumes of ozone. Is this fact in accord with Avogadro's law?

7. If you knew the molecular weight of a gaseous element or compound, how could you determine the approximate weight of 1 liter of the gas?

8. The gas methane is the chief constituent of natural gas. Its molecular weight is 16. (*a*) Calculate the weight of 1 liter of the gas. (*b*) Compare your result with that given in Appendix E for the weight of 1 liter of methane. (*c*) If the two figures are not identical, how do you account for the difference? (*d*) Which is the more accurate?

9. Which of the following statements are true and which false? (*a*) Equal volumes of all elements and compounds measured under the same conditions of temperature and pressure contain the same number of molecules. (*b*) Ozone contains 3 atoms in each molecule, while oxygen contains only 2. (*c*) 2 volumes of hydrogen unite with 1 volume of oxygen to form water; therefore the molecule of hydrogen must contain 2 atoms. (*d*) Avogadro's law applies only to gases and vapors.

10. Avogadro thought that equal volumes of all gases, measured under the same conditions of temperature and pressure, contain the same number of molecules. (*a*) Was he able to prove that this is so? (*b*) If not, why do you suppose he believed the statement to be true?

OPTIONAL EXERCISES

1. Prepare a statement of all the laws we have so far studied, giving the name of each.

2. By experiment it was found that 12 g of a certain nonelectrolyte, dissolved in 200 ml of water, lowered the freezing point of the water 0.374°. Calculate the molecular weight of the compound.

CHAPTER XVI

Formulas and Equations

[New Meanings for Symbols and Formulas]

FORMULAS

The origin of symbols and formulas. The alchemists used very complicated symbols to represent the elements. Copper, for example, was represented by the looking-glass of Venus (thus: ♀), because Venus was supposed to have arisen from the waters near Cyprus, which had great copper mines. Dalton used simpler symbols (Fig. 137), but these were still too complicated.

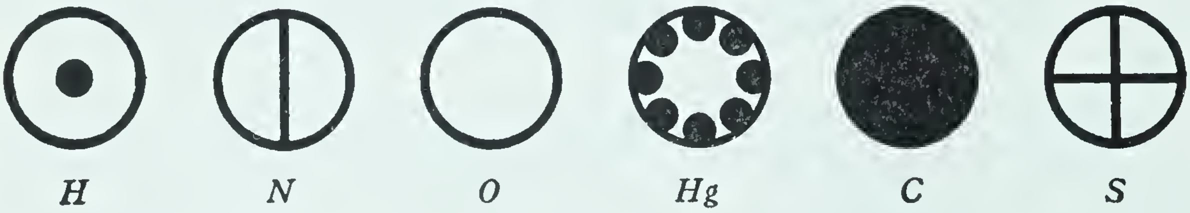


FIG. 137. Samples of symbols used by Dalton to represent the different elements

So the great Swedish chemist Berzelius (Fig. 138) started the custom of using one or two letters from the name of the element, as we do today. As the number of compounds increased, a new use was found for symbols: they were combined in formulas to replace all sorts of names, such as *blue vitriol* or *corrosive sublimate.*

New meanings for symbols and formulas. We learned (p. 32) that the symbol of an element stands not only for the element but for a definite amount of it, namely, 1 atom. So, too, the formula of a compound stands for 1 molecule of the compound.

Now that we have learned about atomic weights and molecular weights, we may go a step farther and say that the symbol of an element stands not only for 1 *atom* of the element but for the relative weight of the atom as expressed by its atomic weight. Thus the symbol O represents 1 atom of oxygen, weighing 16.

Since the symbol of an element represents the *weight* of the atom, the formula of a compound must represent not only the molecule of the compound but also its weight. In the formula H_2O the oxygen atom weighs 16, and each hydrogen atom 1.008; so the formula of water, H_2O, represents one molecule of water weighing $(2 \times 1.008) + 16$, or 18.016. The formula of carbon dioxide, CO_2, represents 1 atom of carbon, weighing 12.01, and 2 atoms of oxygen, each weighing 16. This gives a total of 44.01 for the weight of the molecule of carbon dioxide. So the formula CO_2 represents one molecule of carbon dioxide, weighing 44.01, as compared with the oxygen molecule, weighing 32, which is our standard.

FIG. 138. Jöns Jacob Berzelius (1779–1848)

A great Swedish chemist who originated the custom of representing the atoms of elements by the system of symbols we now use. He discovered a number of elements and made many contributions to our knowledge of chemistry

How we get formulas. When we find a new compound, we first analyze it or else make it by synthesis, and so get its *percentage* composition, as in the case of water. Thus we found water to be 11.19 per cent hydrogen and 88.81 per cent oxygen (p. 130); that is, there are 11.19 g of hydrogen and 88.81 g of oxygen in 100 g of water.

Now these percentage figures represent *parts in 100* of water; but the chemist wants to know how many *atoms* of each element there are in a *molecule* so that he can give the compound a formula. It is not at all hard to solve this problem. Let us divide the number of grams of each element in 100 g of a compound by the atomic weight of that element (that is, by the relative weight of its atoms). The quotients will be *the relative numbers of the several kinds of atoms* in the compound, and so in its molecule.

Example 1. *Determine the simplest formula for water.* Let us follow this plan to find a formula for water.

Hydrogen: 11.19 ÷ 1.008 (at. wt. of hydrogen) = 11.10
Oxygen: 88.81 ÷ 16 (at. wt. of oxygen) = 5.55

This shows that there are *relatively* 11.10 atoms of hydrogen and 5.55 atoms of oxygen in the molecule of water. To get the *simplest* ratio, we divide each of these numbers by the smaller (5.55) and get the ratio 2 : 1, or 2 atoms of hydrogen to 1 of oxygen. This tells us that the molecule of water contains twice as many atoms of hydrogen as of oxygen. Evidently the *simplest* formula for water is H_2O.

Is H_2O the true formula? But other formulas are possible, such as H_4O_2, H_6O_3, H_8O_4. All these have twice as many atoms of hydrogen as of oxygen, but each has a different molecular weight, as follows:

FORMULA	WEIGHT OF HYDROGEN PRESENT		WEIGHT OF OXYGEN PRESENT		MOLECULAR WEIGHT RESULTING
H_2O	2 × 1.008	+	16	=	18.016
H_4O_2	4 × 1.008	+	2 × 16	=	36.032
H_6O_3	6 × 1.008	+	3 × 16	=	54.048
H_8O_4	8 × 1.008	+	4 × 16	=	72.064

Now experiments show that 22.4 liters of steam weighs approximately 18 g, so that the molecular weight of water must be about 18. The correct formula for water, then, must be H_2O, since this is the only one of the possible formulas that agrees with the molecular weight of water as found by experiment.

Formulas, like that of water, that represent the composition of a molecule are sometimes called *molecular formulas*, to distinguish them from certain other kinds of formulas that we may meet from time to time; for we use different kinds of formulas to express different experimental facts.

Example 2. *The formula for mercuric oxide.* As a second example let us find the formula for mercuric oxide. Its percentage composition as found by analysis is mercury 92.6 per cent and oxygen 7.4 per cent. Dividing each of these numbers by the atomic weight of the corresponding element, we have the following quotients:

Mercury: 92.6 ÷ 200.61 (at. wt. of Hg) = 0.461
Oxygen: 7.4 ÷ 16 (at. wt. of O) = 0.462

The ratio of atoms of mercury to oxygen in the molecule of mercuric oxide is therefore 1 : 1, so that the formula for mercuric oxide must be HgO or some multiple of this. Now mercuric oxide is a crystalline solid and so has no simple molecular weight (p. 49). *In all such cases we keep the simplest formula that the compound could have.* This gives us the formula HgO for mercuric oxide.

While the formulas derived from percentage composition alone, as in the case of mercuric oxide, are not necessarily molecular formulas, yet for all practical purposes we may take them as such. For, like molecular formulas, they represent the elements present in a compound, as well as the ratios in which the atoms of the different elements are combined.

Summary: steps in finding formulas. These, then, are the steps in finding the formula of a compound: (1) find the percentage composition of the compound by experiment; (2) from the percentage composition calculate the *relative* number of the different kinds of atoms in the molecule, and the possible formulas that the compound may have; (3) find the molecular weight by experiment; (4) knowing the molecular weight, select the correct formula. In case no methods are known for measuring the molecular weight of the compound, keep the simplest possible formula.

Percentage composition from formulas. We can get the formula of a compound from its percentage composition. Having once found the formula, it is an easy matter to turn the formula back into the percentage composition of the compound.

Example. Zinc sulfate: formula $ZnSO_4$

Zinc, 1 atom	65.38
Sulfur, 1 atom	32.06
Oxygen, 4 atoms	64.00
Total weight	161.44

Of this total weight 65.38 parts are zinc, 32.06 parts are sulfur, and 64 parts are oxygen:

65.38/161.44 is zinc,	or	40.50%
32.06/161.44 is sulfur,	or	19.86%
64/161.44 is oxygen,	or	39.64%
	Total,	100.00%

Formulas of hydrates. Many compounds form hydrates when crystallized from water solution (p. 116). In these a definite number of water molecules combine with one or more molecules of the compound. These hydrates are given formulas by writing the formula of the compound and that of water, separated by a point (·) and with the appropriate coefficient. The formula of the hydrate of zinc sulfate is $ZnSO_4 \cdot 7\,H_2O$; that of the hydrate of calcium chloride is $CaCl_2 \cdot 6\,H_2O$.

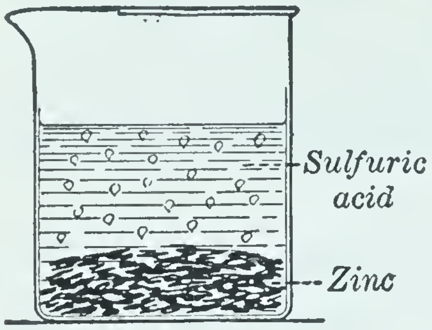


Fig. 139. Sulfuric acid acting upon pieces of zinc

EQUATIONS

Chemical equations. Having found a way to show the composition of molecules (and therefore of masses of molecules) by formulas, the chemist goes a step farther and uses these formulas to give the facts of a chemical change in very brief form. He calls such a change a *chemical reaction.*

For example, we may imagine a beaker containing pieces of zinc to which sulfuric acid has been added, producing zinc sulfate and hydrogen (Fig. 139). We may describe this reaction in a word equation in this way:

Word equation:

Zinc + sulfuric acid ⟶ zinc sulfate + hydrogen

But the reaction really takes place between atoms and molecules, for all of which we have formulas. We can write the same facts in a *formula* equation, as follows:

Formula equation:

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$$

We write hydrogen H_2 and not 2 H, because we have found that hydrogen gas consists of molecules, each of which contains 2 atoms (p. 183). Zinc is a solid, and we give it the simplest possible formula (p. 189).

We place a vertical arrow (↑) following the formula of hydrogen (H_2) to indicate that hydrogen is a gas and, under ordinary conditions, will be given off in that form.

Balancing an equation. Chemical formulas show not only the elements in the molecule but *the relative weights of the atoms and molecules as well.* So every correct equation must *balance*; that is, it must have as many atoms of each kind on one side of the arrow as on the other side. The equation just given balances as it stands. Many others must be balanced.

When an equation does not balance, it will not do to change a formula; for formulas are found by experiment and express *facts.* It must be balanced by changing the *number* of molecules taking part in the reaction. The following examples will show how this is done.

Example 1. Let us find the equation for the action of hydrochloric acid on zinc.

Word equation:

Zinc + hydrochloric acid ⟶ zinc chloride + hydrogen

Formula equation: $Zn + HCl \longrightarrow ZnCl_2 + H_2\uparrow$
Balanced equation: $Zn + 2\ HCl \longrightarrow ZnCl_2 + H_2\uparrow$

Example 2. *Equation for the burning of the metal magnesium in air.* Both magnesium and its oxide, MgO, are solids. Keep in mind that the oxygen molecule, like the hydrogen molecule, consists of 2 atoms.

Word equation: Magnesium + oxygen ⟶ magnesium oxide
Formula equation: $Mg + O_2 \longrightarrow MgO$
Balanced equation: $2\ Mg + O_2 \longrightarrow 2\ MgO$

Equations of reactions so far studied. Let us now write the first three steps in making the equations for some of the important reactions so far studied. *Remember that in each case the balanced equation is the correct one.*

Preparation of oxygen. 1. From potassium chlorate.

Word equation:

Potassium chlorate ⟶ potassium chloride + oxygen

Formula equation: $KClO_3 \longrightarrow KCl + O_2\uparrow$
Balanced equation: $2\ KClO_3 \longrightarrow 2\ KCl + 3\ O_2\uparrow$

2. From the electrolysis of water.

Word equation: water ⟶ hydrogen + oxygen
Formula equation: $H_2O \longrightarrow H_2\uparrow + O_2\uparrow$
Balanced equation: $2\ H_2O \longrightarrow 2\ H_2\uparrow + O_2\uparrow$

Preparation of hydrogen. 1. From sodium and water.

Word equation:

Sodium + water ⟶ sodium hydroxide + hydrogen

Formula equation: $Na + H_2O \longrightarrow NaOH + H_2\uparrow$
Balanced equation: $2\ Na + 2\ H_2O \longrightarrow 2\ NaOH + H_2\uparrow$

2. From zinc and sulfuric acid.

Word equation:

Zinc + sulfuric acid ⟶ zinc sulfate + hydrogen

Formula equation: $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$
Balanced equation: $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$

3. From iron and steam.

Word equation: Iron + steam ⟶ iron oxide + hydrogen
Formula equation: $Fe + H_2O \longrightarrow Fe_3O_4 + H_2\uparrow$
Balanced equation:

$$3\ Fe + 4\ H_2O \longrightarrow Fe_3O_4 + 4\ H_2\uparrow$$

Preparation of hydrogen peroxide. From barium peroxide and sulfuric acid.

Word equation:

Barium peroxide + sulfuric acid
⟶ barium sulfate + hydrogen peroxide

Formula equation: $BaO_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow + H_2O_2$
Balanced equation: $BaO_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow + H_2O_2$

It will now be clear why we write the formula of hydrogen peroxide H_2O_2 rather than HO (p. 133). If it were HO, the molecular weight would be 17; if H_2O_2, the molecular weight would be 34. Experiment shows that it really is 34; so the formula H_2O_2 is the correct one.

Gram-molecular (or formula) weights; gram-atomic (or symbol) weights. We have learned that the equation

$$\underset{65.38}{Zn} + \underset{98.076}{H_2SO_4} \longrightarrow \underset{161.44}{ZnSO_4} + \underset{2.016}{H_2}\uparrow$$

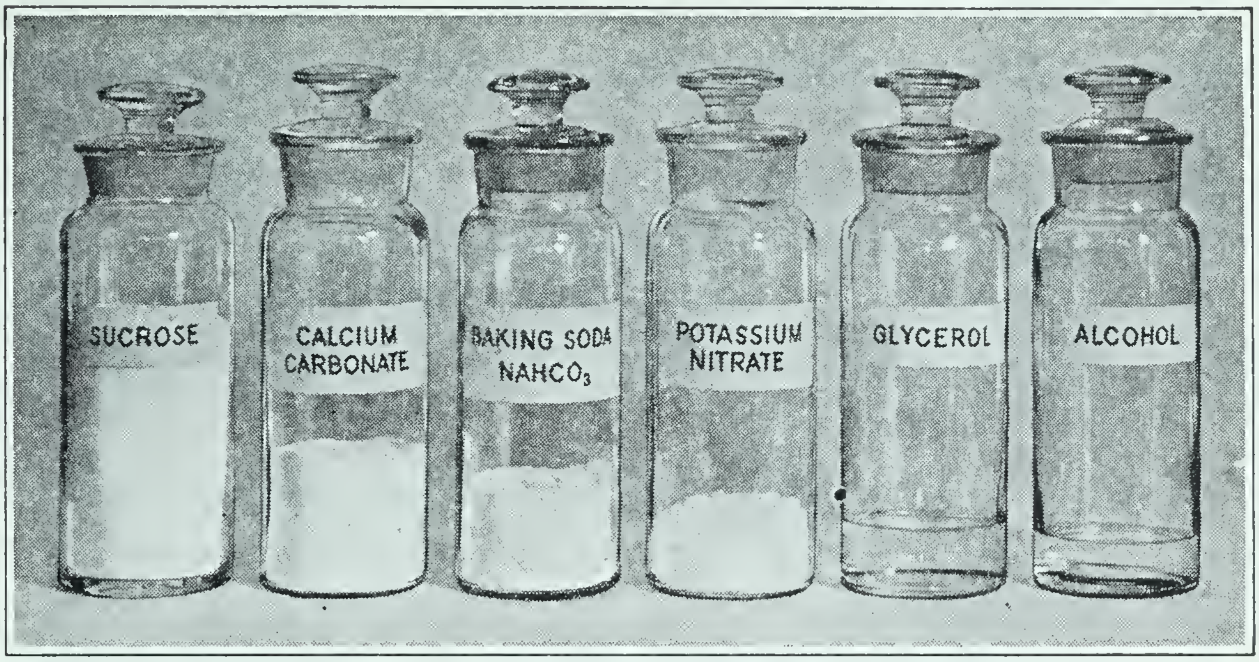


FIG. 140. Gram-molecular weights

The picture shows the gram-molecular weights of the following compounds: sucrose (common sugar) ($C_{12}H_{22}O_{11}$); calcium carbonate ($CaCO_3$); baking soda ($NaHCO_3$); potassium nitrate (KNO_3); glycerol ($C_3H_8O_3$); alcohol (C_2H_6O). Calculate the number of grams in each bottle

tells us that 1 atom of zinc requires 1 molecule of sulfuric acid to complete a reaction that produces 1 molecule of zinc sulfate and 1 molecule of hydrogen.

The weight of the zinc atom and that of the molecule of sulfuric acid are different, and their relative weights are placed below the formula in the equation. To bring together just the right weights of zinc and of sulfuric acid for the reaction, we must weigh them out in the ratio 65.38 : 98.076, *not* in the ratio of the numbers before the formulas (1 : 1).

Since the chemist weighs his material in *grams*, we say that we use zinc and sulfuric acid in the proportion 65.38 *grams* of zinc to 98.076 *grams* of sulfuric acid. This gram-weight corresponding to the formula of a compound is called its gram-molecular (or molar) weight.

The gram-molecular (or molar) weight of any compound is the weight in grams corresponding to the sum of the atomic weights in its formula (Fig. 140).

The gram-atomic (or symbol) weight of any element is the weight in grams corresponding to its atomic weight.

Thus, the gram-molecular weight of sulfuric acid (H_2SO_4) is 98.076 g, and that of water is 18.016 g. The gram-atomic weight of hydrogen is 1.008 g, and that of zinc is 65.38 g.

Gram-molecular (or molar) solutions. In stating the concentration of a solution we may, of course, make use of the percentage system; but it is often much better to state the number of gram-molecular weights of the compound which a given volume of the solution contains.

A gram-molecular (or molar) solution of a compound is one that contains 1 gram-molecular weight of the compound in 1 liter of the solution.

Thus a gram-molecular solution of sodium chloride ($NaCl$) contains 22.997 g + 35.457 g, or 58.454 g, of the chloride in 1 liter of the solution.

For a discussion of *normal solutions*, see Appendix, p. 642.

Various meanings of equations. Let us write the equation

$$Zn + 2\ HCl \longrightarrow ZnCl_2 + H_2 \uparrow$$

It will be seen that such an equation states three kinds of facts and may be read in three ways.

1. *Substance fact:* zinc acts upon hydrochloric acid, forming zinc chloride and hydrogen.

2. *Molecular fact:* 1 atom of zinc acts upon 2 molecules of hydrochloric acid, and forms 1 molecule of zinc chloride and 1 molecule of hydrogen.

3. *Weight fact:* 1 gram-atomic weight of zinc (65.38 g) acts upon 2 gram-molecular weights of hydrochloric acid (2 × 36.47 g), and forms 1 gram-molecular weight of zinc chloride (136.29 g) and 1 gram-molecular weight of hydrogen (2.02 g).

Types of reactions. A careful study of the reactions we have had so far will show that they are of four kinds: (1) *combination*, (2) *decomposition*, (3) *simple replacement*, (4) *double replacement*. Nearly all the reactions we shall study belong to one or other of these four types.

1. ***Reactions of combination.*** Reactions of combination are those in which two elements unite to form a compound. This is illustrated in the formation of water from oxygen and hydrogen:

$$2\ H_2 + O_2 \longrightarrow 2\ H_2O$$

2. ***Reactions of decomposition.*** Reactions of decomposition are those in which a compound breaks down to form

other things, either elements or compounds. All the reactions for the preparation of oxygen are illustrations of decomposition.

$$2\ HgO \longrightarrow 2\ Hg + O_2\uparrow$$

3. *Simple replacement.* In reactions of simple replacement some one element in a compound is replaced by another free element. In all the reactions for the preparation of hydrogen, the hydrogen in the acids or in water is replaced by a metal, and the hydrogen is set free:

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$$

4. *Double replacement.* In reactions of double replacement *two* elements in *two different compounds* exchange places. This is illustrated in the preparation of hydrogen peroxide, in which reaction the barium of the oxide and the hydrogen of the acid exchange places:

$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow + H_2O_2$$

CHAPTER SUMMARY IN QUESTION FORM

1. (*a*) What different meanings may the symbol of an element have? (*b*) Illustrate in the case of oxygen.

2. (*a*) What different meanings may the formula of a compound have? (*b*) Illustrate in the case of water.

3. State what each of the following symbols and formulas represents: O, H, H_2O, Hg, K, Cl, H_2SO_4, HCl.

4. A molecule of sugar contains 12 atoms of carbon, 22 atoms of hydrogen, and 11 atoms of oxygen. Write its formula.

5. State how many atoms of oxygen are present in each of the following: CO_2, 2 CO, Fe_3O_4, 2 $AgNO_3$, 3 C_2H_6O.

6. (*a*) What information must you have about a compound in order to find its formula? (*b*) Illustrate by showing how the formula of water is found.

7. (*a*) Suppose you know the percentage composition of a compound which forms no simple molecule, or, if it does form one, whose molecular weight is unknown. What kind of formula shall we choose for the compound? (*b*) Illustrate in the case of mercuric oxide.

8. Knowing the percentage composition and the molecular weight of a compound, you can get its formula. But suppose

you are given the formula of a compound. From this formula can you calculate the percentage composition and molecular weight of the compound?

9. The formula for water is H_2O. Knowing this fact, and the atomic weights of hydrogen and oxygen, calculate the percentage composition and the molecular weight of water.

10. Give the steps in writing an equation, using as an illustration the equation representing (*a*) the decomposition of potassium chlorate by heat; (*b*) the action of hydrochloric acid on zinc.

11. (*a*) What do you understand by the term *gram-atomic* (or *symbol*) *weight* of an element? (*b*) Give the gram-atomic weight of the following elements: oxygen; carbon; iron.

12. (*a*) What do you understand by the term *gram-molecular* (or *formula*) *weight* of a compound? (*b*) Calculate the gram-molecular weight of each of the following compounds: water (H_2O); alcohol (C_2H_6O); sugar ($C_{12}H_{22}O_{11}$).

13. Write the equation showing the reaction of hydrochloric acid on zinc, and state three kinds of facts that the equation shows.

14. (*a*) Reactions are of how many types? (*b*) Illustrate each type by an example.

THOUGHT QUESTIONS

1. Does a formula tell us anything that someone did not first have to find out by experiments?

2. In a vertical column write the formulas for the compounds having the following composition: (*a*) 2 atoms of hydrogen, 1 of sulfur, and 4 of oxygen; (*b*) 1 atom of mercury and 1 of oxygen; (*c*) 1 atom of carbon and 2 of oxygen; (*d*) 2 atoms of iron and 3 of oxygen; (*e*) 2 atoms of carbon, 6 of hydrogen, and 1 of oxygen.

3. Opposite each formula of question 2 write (*a*) the total number of atoms present in the molecule; (*b*) the molecular weight of each compound.

4. (*a*) Calculate the percentage composition of hydrogen sulfate (H_2SO_4). (*b*) Compare your results with those given on page 104.

5. A compound was found on analysis to contain 5.93 per cent of hydrogen and 94.07 per cent of oxygen. Experiments proved its molecular weight to be approximately 34. Calculate (*a*) its simplest formula and (*b*) its correct formula.

6. Copy the following table and fill in the blank spaces:

PERCENTAGE COMPOSITION OF COMPOUND	RELATIVE NUMBER OF ATOMS IN THE MOLECULE	SIMPLEST RATIO	SIMPLEST FORMULA
Hydrogen 2.76%			
Chlorine 97.24%			
Sodium 39.34%			
Chlorine 60.65%			
Potassium 38.69%			
Nitrogen 13.88%			
Oxygen 47.45%			

7. The simplest formula of a compound calculated from its percentage composition is CH. Its molecular weight is found to be 78. Find the correct formula.

8. (*a*) Calculate the per cent of carbon and of hydrogen in the compound referred to in problem 7. (*b*) Will the per cent of carbon and hydrogen in the simplest formula be the same as in the correct formula?

9. Balance the following equations:

$Hg + O_2 \longrightarrow HgO$

$H_2 + O_2 \longrightarrow H_2O$

$Zn + HCl \longrightarrow ZnCl_2 + H_2$

$BaO_2 + HCl \longrightarrow BaCl_2 + H_2O_2$

$Na + HCl \longrightarrow NaCl + H_2$

OPTIONAL EXERCISES

1. Ethylene, a gaseous compound used as an anesthetic by surgeons, was found on analysis to have the following percentage composition: carbon, 85.7 per cent; hydrogen, 14.3 per cent. 1 liter of the gas was found to weigh 1.25 g. Calculate its formula.

2. Ordinary alcohol has the following composition: carbon, 52.12 per cent; hydrogen, 13.13 per cent; oxygen, 34.74 per cent. Its molecular weight is approximately 46. (*a*) Calculate its simplest formula. (*b*) Calculate its correct formula.

3. Is there any difference between 2 H and H_2? between 2 NO_2 and N_2O_4?

4. A student asked the following question: "I do not see why it is necessary for the chemist to carry on a lot of experiments in order to get the molecular weight of a compound. Why does he not simply add up the weights of the atoms present in the formula of the compound?" What answer would you give to this question?

CHAPTER XVII

Valence

[How Atoms Fit Together]

Still another number ratio. In our study of atoms we learned that they combine with each other in definite ratios by weight. If we study the formulas and equations we have been using, we shall learn another important fact. Just as we can give each atom of an element a *weight* that shows *how much* of that element will take part in a reaction with another element, so we can give each atom a *number* that shows *how many* of its atoms will combine with an atom of some other element. We call this number the *valence* of the atom.

The valence of atoms. The best way to get a clear idea of valence is to study an equation. So let us take the equation found on page 149:

$$CaCO_3 + 2\,HCl \longrightarrow CaCl_2 + H_2O + CO_2 \uparrow$$

We see that 1 atom of hydrogen combines with 1 atom of chlorine (HCl), while 1 atom of calcium combines with 2 atoms of chlorine ($CaCl_2$). And while 1 atom of chlorine combines with 1 atom of hydrogen (HCl), 1 atom of oxygen combines with 2 atoms of hydrogen (H_2O). Later on we shall find that 1 atom of nitrogen combines with 3 atoms of hydrogen (NH_3), while 1 atom of carbon combines with 4 atoms of hydrogen (CH_4). So we have the compounds

$$HCl,\ H_2O,\ H_3N,\ H_4C$$

Take another example of this number ratio. When sodium acts upon sulfuric acid, 1 atom of sodium displaces 1 atom of hydrogen, but when zinc acts on sulfuric acid, 1 atom of zinc displaces 2 atoms of hydrogen:

$$2\,Na + H_2SO_4 \longrightarrow Na_2SO_4 + H_2 \uparrow$$
$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2 \uparrow$$

The valence of an atom is the number of hydrogen atoms it can hold in combination or displace from a compound.

Why we take hydrogen as a standard for valence. A study of the formulas of all the compounds of hydrogen with other elements shows an interesting thing: One atom of hydrogen never combines with more than one atom of any other element. It is for this reason we take it as our standard in the definition of valence. The element chlorine (Cl) seldom combines with more than one atom of another element. So we can usually tell the valence of an element either from the formula of its hydrogen compound or from that of its chlorine compound. For example, hydrogen forms no compound with aluminum (Al), but chlorine forms the compound $AlCl_3$. From this we see that the valence of aluminum is 3.

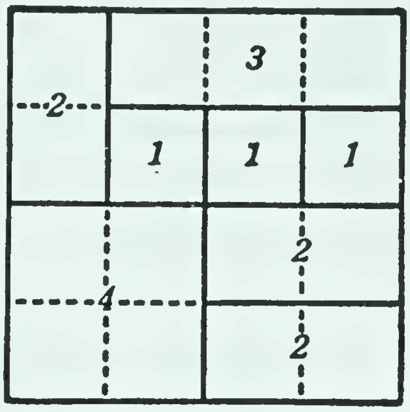


FIG. 141. Illustration of valence

How we name valences. Atoms, like hydrogen and chlorine, that can hold in combination only one atom of any other element are called *univalent* atoms. Oxygen, sulfur, zinc, and iron, whose atoms combine with two of hydrogen or of chlorine, are called *bivalent* atoms. There are other elements whose atoms have still higher valences — of three (*trivalent*), four (*quadrivalent*), and so on up to a valence of eight.

A possible misunderstanding. From all that has been said, it might be supposed that the atoms of both copper and oxygen are univalent in the compound CuO, because there is one of each in the molecule. But *measured by hydrogen*, which is our standard, oxygen is bivalent (H_2O); so copper must be bivalent also, a fact which is shown in the formula for its chloride, $CuCl_2$. To find the valence of an atom from the formula of its oxide, always remember that oxygen is *bivalent.*

Illustration of valence. The valence of atoms may be illustrated by the way in which various sizes of tile fit together in a tile floor (Fig. 141). The small squares (1) correspond to the univalent atoms, like hydrogen. It takes two of these to fit beside a rectangular tile (2), which is like oxygen in H_2O. Two rectangular tiles (2) fit together, though each is bivalent, like CuO, while four univalent squares fit the large square (4), like CH_4. Two rectangles (2) fit the large square (4), like CO_2. Three univalent squares fit the large rectangular square (3), like NH_3.

Of course, this illustration does not mean that valence depends on the *size* of the atoms, but is intended merely to show how we choose a standard valence 1 and compare the valence of other atoms with this standard.

Three useful rules of valence. There are three rules of valence that are very useful in writing the correct formulas for compounds.

Rule 1. If two atoms of the same valence combine to form a compound, they will combine atom for atom. This is shown in the following formulas, in which the valence of the atom of each element is marked by the figure above its symbol:

$$\overset{1}{\mathrm{H}}\overset{1}{\mathrm{Cl}},\ \overset{2}{\mathrm{Hg}}\overset{2}{\mathrm{O}},\ \overset{3}{\mathrm{Al}}\overset{3}{\mathrm{N}},\ \overset{4}{\mathrm{Si}}\overset{4}{\mathrm{C}}$$

Rule 2. If two atoms of different valences combine to form a compound, then we must take such numbers of the two kinds of atoms as will add up an equal number of valence units. This is shown in the following formulas:

$$\overset{1}{\mathrm{H}}_2\overset{2}{\mathrm{O}},\ \overset{3}{\mathrm{N}}\overset{1}{\mathrm{H}}_3,\ \overset{4}{\mathrm{C}}\overset{1}{\mathrm{H}}_4,\ \overset{4}{\mathrm{C}}\overset{2}{\mathrm{O}}_2,\ \overset{3}{\mathrm{Al}}_2\overset{2}{\mathrm{O}}_3$$

In the water molecule, H_2O, there is 1 atom of oxygen (2 valences); so there must be two hydrogen atoms in each molecule to add up 2 valences. Again, in the formula CO_2 the carbon is quadrivalent (as shown in the formula CH_4). So for each atom of carbon (4 valences) there must be 2 atoms of oxygen (4 valences).

Rule 3. In any reaction of simple replacement or of double replacement (p. 195) the exchange must be between such numbers of atoms as will add up an equal number of valence units. For example, one bivalent atom will replace two univalent atoms, while two trivalent atoms (6 valences) will replace three bivalent atoms (6 valences).

$$2\,\overset{1}{\mathrm{Na}} + \overset{1}{\mathrm{H}}_2\mathrm{SO}_4 \longrightarrow \mathrm{Na}_2\mathrm{SO}_4 + \mathrm{H}_2\uparrow$$

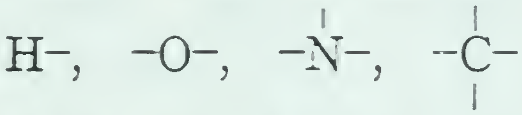
$$\overset{2}{\mathrm{Zn}} + 2\,\overset{1}{\mathrm{H}}\mathrm{Cl} \longrightarrow \mathrm{ZnCl}_2 + \mathrm{H}_2\uparrow$$

$$\overset{1}{\mathrm{Na}}\mathrm{OH} + \overset{1}{\mathrm{H}}\mathrm{Cl} \longrightarrow \mathrm{NaCl} + \mathrm{HOH}\ (\text{or } \mathrm{H}_2\mathrm{O})$$

$$\overset{2}{\mathrm{Ba}}\mathrm{O}_2 + \overset{1}{\mathrm{H}}_2\mathrm{SO}_4 \longrightarrow \mathrm{BaSO}_4 + \mathrm{H}_2\mathrm{O}_2$$

Many atoms have more than one valence. As a rule the atoms of any given element do not have one fixed valence. The atoms of most elements have two different valences, and some have more. For example, copper forms two compounds, $CuCl$ and $CuCl_2$, in which the copper atom is univalent in the one and bivalent in the other. Similarly, tin and chlorine form compounds with the formulas $SnCl_2$ and $SnCl_4$. A given atom often has one valence for one kind of atom and a different valence for another. Sulfur is bivalent in the compound H_2S but quadrivalent in the compound SO_2.

Bonds and structural formulas. It is often helpful to show the valences of elements by lines drawn from the symbols of the elements, each line (or *bond*, as it is often called) standing for a single valence. In this way we may represent the valence of hydrogen (univalent), oxygen (bivalent), nitrogen (trivalent), and carbon (quadrivalent) as follows:



$$H-,\quad -O-,\quad -\overset{|}{N}-,\quad -\underset{|}{\overset{|}{C}}-$$

In a molecule of water (H_2O) we have every reason for believing that each of the two atoms of hydrogen is combined directly with oxygen. This fact can be expressed by the formula $H-\;-O-\;-H$ or, more simply, $H—O—H$, in which the two valences of the hydrogen atoms *saturate* the two valences of the oxygen atom. Such a formula is called a *structural formula.*

Puzzling cases of valence. In using these rules of valence the student will meet with many cases which are puzzling. For example, in the formula for hydrogen peroxide, H_2O_2, one would be inclined to say that oxygen and hydrogen have the same valence; and the formula for iron oxide, Fe_3O_4, would indicate that the iron atom has a valence of $2\frac{2}{3}$, which evidently cannot be the fact. Puzzling cases of this kind will become clear in later chapters.

HOW DO WE EXPLAIN VALENCE?

Valence and atomic structure. So far we have been thinking of valence merely as an experimental fact and have made no attempt to account for it. The facts will always be as we have described them; but we want to know *why* they are so — why hydrogen is univalent and oxygen bivalent. It is reasonable to suppose that the facts of valence are to be explained by the structure of the atoms. Let us now see if this is true.

Atoms of no affinity or valence. In our study of the structure of the atom we learned that the electrons revolve in orbits around the nucleus; that the first orbit is completely filled with 2 electrons, the second one with 8, and the third one with 8. This fact is so important that we give a special name to the *outside* orbit (of 8 electrons when completed) and call it the *octet* of the atom.

Now experiment has shown that those atoms which have completed octets (with rare exceptions) never combine with other atoms nor with each other. They have no affinity for anything, and no valence. They are all gases which are made up of uncombined atoms. There are six of these elements: helium, neon, argon, krypton, xenon, and radon. We shall study their properties in a later chapter.

The clue to chemical affinity. While all atoms with completed octets have neither affinity nor valence, *all atoms with incomplete octets have both.* This gives us the clue to the secret of affinity and valence. *Chemical action is due to the tendency of as many atoms as possible to complete their octets.* There are two general ways in which completed octets may be formed, and these will now be described.

Octets completed by gain or loss of electrons — electrovalent, or polar, compounds. An atom may surrender one or more electrons from its incomplete octet and so trim itself back to the completed orbit behind the incomplete one. Or it may capture from some other atom enough electrons to fill out its incomplete octet.

For example, the lithium atom (Fig. 142), with only one electron in its octet orbit, may hand over this lone electron to some other atom whose outer orbit is nearly complete — say, to a fluorine atom, which needs but one more. We may represent this completed reaction by Fig. 142. The lithium atom, having *lost* one electron, now has merely its completed inner orbit of 2 electrons (like helium), but is *positive* (+)

by one unit charge, since it has one more proton than electron. The fluorine atom has *gained* one electron, completing its outer orbit of eight electrons (like neon), and is now *negative* (–) by one charge. The two modified atoms, one positive and the other negative, are attracted to each other and held together by these opposite charges.

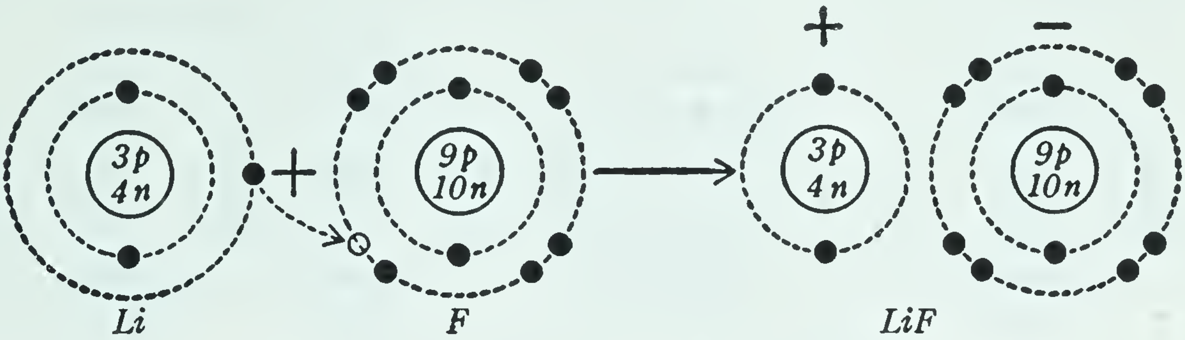


FIG. 142. The reaction Li + F ⟶ LiF

The sodium atom, like the lithium atom, has one lone electron in its octet orbit (Fig. 143), while the oxygen atom has six, and so needs two more to complete this orbit. We may represent the action of sodium on oxygen as follows:

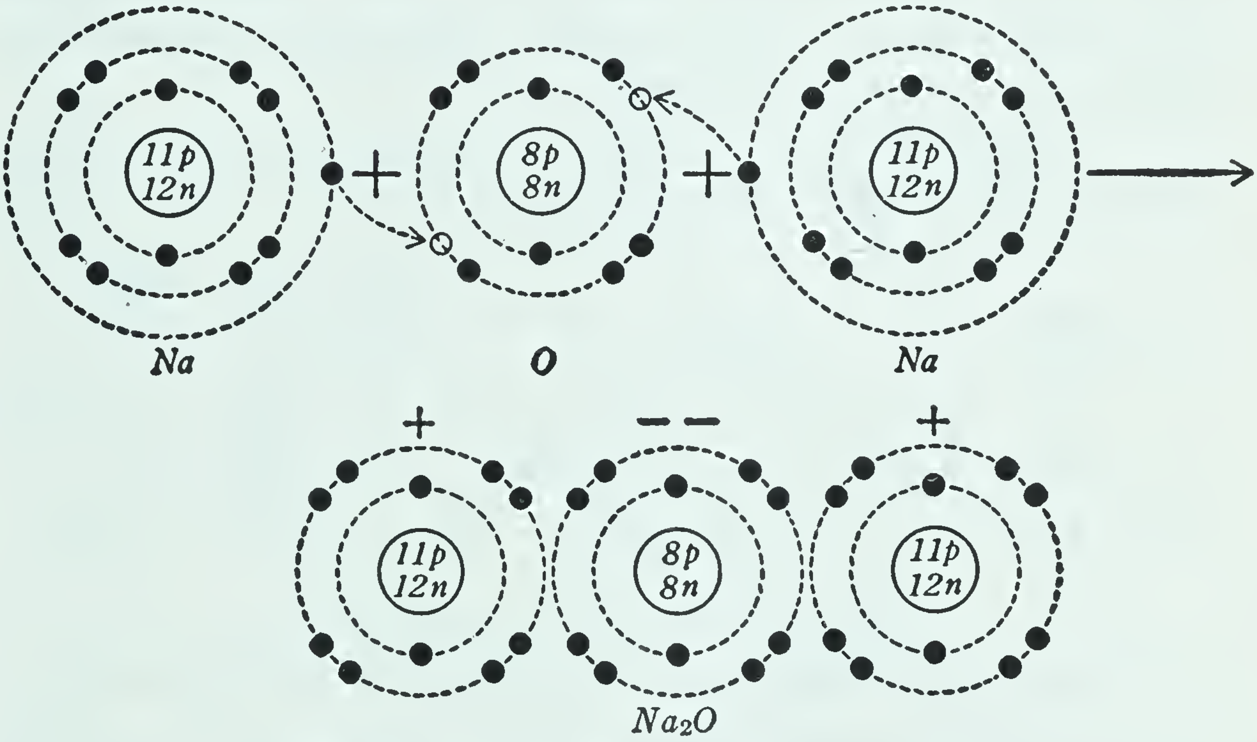


FIG. 143. The reaction 2 Na + O ⟶ Na_2O

Each of the two atoms of sodium has *surrendered* the lone electron in its outer orbit to the oxygen atom, and is left with a completed octet (like neon); and each is *positive* by one charge. The oxygen atom has *captured* these two electrons and has filled up the two vacant places in its octet. It has a complete octet (like neon), and is negative by two charges. The three atoms just balance each other electrically and are attracted to each other by their opposite charges. *Compounds formed by give and take of electrons are called electrovalent or polar compounds.* They are electrolytes.

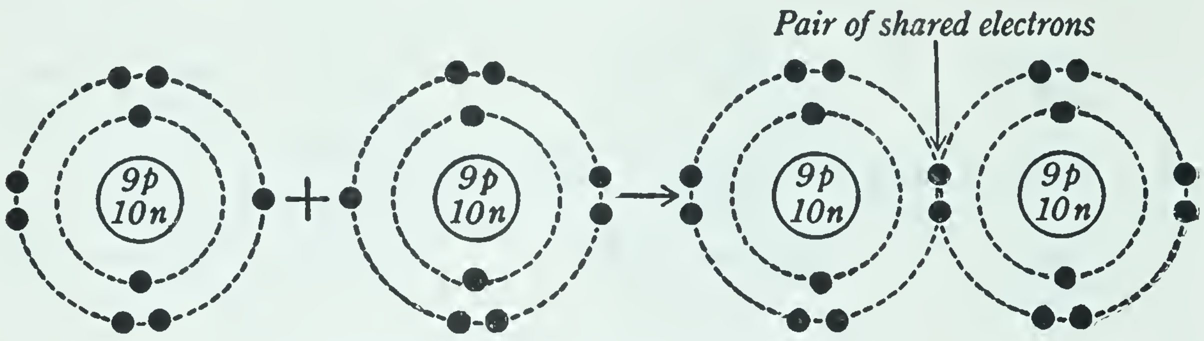


Fig. 144. The reaction $F + F \longrightarrow F_2$

Two atoms of fluorine share a pair of electrons to form a covalent molecule

Octets completed by sharing pairs of electrons — covalent, or nonpolar, compounds. Instead of surrendering or capturing electrons, two atoms may pool some of their electrons. Each atom may contribute one electron to make a *pair*, or two electrons to make *two pairs.* The two atoms hold these pairs *in common*, and each atom counts both electrons of a pair in its octet.

For example, when two atoms of fluorine combine to form a molecule, the two atoms share one pair of electrons, as shown in Fig. 144. Likewise two atoms of oxygen share two pairs of electrons to form a molecule (Fig. 145). In both cases the octet of each atom is complete.

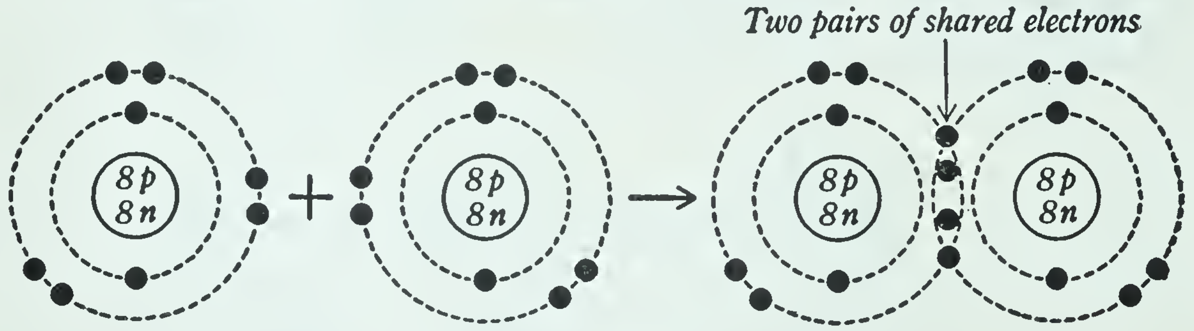


Fig. 145. The reaction $O + O \longrightarrow O_2$

Two atoms of oxygen share two pairs of electrons to form a covalent molecule

Compounds formed by sharing pairs of electrons are called covalent or nonpolar compounds. They are nonelectrolytes.

Atoms that lend, borrow, or share. Atoms with only one, two, or sometimes three electrons in their outer orbit (like hydrogen, sodium, and magnesium) tend to *lose* electrons and may be called *lending* atoms. They are nearly all atoms of metals. Atoms that lack only one, two, or even three electrons in their outer orbit (like fluorine, chlorine, and oxygen) tend to capture electrons and are called *borrowing* atoms. They are all atoms of nonmetals. It is largely the atoms that lack three, four, or five electrons in their outer orbit (like nitrogen, carbon, and phosphorus) that form *covalent* compounds.

Atomic structure and valence. We can now see a very good reason for valence. *The valence of an atom is due to loss or gain of electrons or to sharing them in pairs.* The atom that loses or gains one electron during chemical change, or shares a pair with another atom, is a *univalent* atom; while one which loses or gains two electrons, or shares two pairs, is a *bivalent* atom. It is also clear why valence is a *number* ratio and can always be expressed by a whole number. An atom cannot lose or gain a fraction of an electron, for electrons are indivisible.

Positive and negative valence. We often want to state briefly whether the valence of an atom is due to the *loss* or to the *gain* of an electron. So we say that an atom which tends to lose electrons (and so becomes positive) has a *positive valence* of 1, 2, or 3, depending upon the number of electrons lost. An atom that tends to borrow electrons (and so becomes negative) has a *negative valence* of 1, 2, or 3, depending upon the number of electrons gained.

It is customary to represent the positive or negative valence of an element by the appropriate sign, + or −. We say that sodium has a valence of + 1, oxygen a valence of − 2, and calcium a valence of + 2. Nitrogen acts in different ways. Under some conditions it borrows 3 electrons, while under other conditions it loses either 3 or 5; so we represent its valence as follows: − 3, + 3, + 5. (See table on page 207.)

Valence electrons. It will be noticed that it is only the electrons in *the outer, incomplete orbits* that are concerned with the chemical conduct of an atom and that give the atom its valence. For this reason the electrons in the outer, incomplete orbits are called the *valence electrons* of the atom.

Variable valence. We can now see why the valence of an atom may be *variable.* An atom with two or three valence electrons may lend sometimes one of these, sometimes two, or even all three, depending upon the urgency of the need of the borrowing atom. Atoms that lack one, two, or three electrons may at times succeed in borrowing all they need, and under other conditions only a part.

Simple methods of representing the structure of atoms and molecules. In writing equations like those in Figs. 144 and 145 we usually adopt a simpler way. It is only the valence electrons that concern us; so we represent the fluorine atom (which has seven valence electrons) by the symbol $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}\cdot$, in which each dot stands for an electron. In the same way the oxygen atom (six valence electrons) is represented by the symbol $:\underset{\cdot\cdot}{O}:$.

The equation in Fig. 144 then becomes

$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}: \longrightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:$$

Or we may represent only the shared electrons and write the equation thus: $F\cdot + \cdot F \longrightarrow F:F$

We often go a step farther and represent a *pair of shared electrons* by a *dash*, in which case the fluorine molecule is represented by F–F.

Likewise we may represent the equation in Fig. 145 in either of the following ways:

$$\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}: + :\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} \longrightarrow \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}::\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}};\quad O: + :O \longrightarrow O::O;\quad \text{or } O=O$$

Atomic structure, and oxidation and reduction. As a partial definition we have said that oxidation is the process of combining with oxygen (p. 88), and reduction the taking of oxygen from a compound (p. 109). Does a knowledge of atomic structure help us to broaden these definitions to include reactions in which oxygen plays no part?

When sodium combines with oxygen, we say it is oxidized, and we may write the equation:

$$2\,Na + O \longrightarrow Na_2O$$

By reference to Fig. 143 it will be seen that what has really happened is that each of two sodium atoms has given up its lone valence electron to an oxygen atom:

$$2\,\dot{\text{Na}} + \cdot\underset{\cdot\cdot}{\ddot{\text{O}}}\cdot \longrightarrow \text{Na}^+,\ :\underset{\cdot\cdot}{\ddot{\text{O}}}:^{--},\ \text{Na}^+$$

Since the sodium atoms have evidently been oxidized, we may say that oxidation is the loss of electrons by an atom (or radical). But at the same time an oxygen atom has *gained* electrons, which is the opposite to oxidation. So we say it has been *reduced*.

In the equation shown in Fig. 142 the lithium atom (Li) has lost an electron and has been oxidized. The fluorine atom (F) has gained an electron and has been reduced.

Oxidation is the losing of one or more electrons by an atom (or radical) during chemical action.

Reduction is the gaining of one or more electrons by an atom (or radical) during a chemical action.

A word about theories. In this picture of the structure of the atom we have another example of a scientific theory. The experimental *facts* cannot well be doubted; but many details of the picture are unsatisfactory, and will undoubtedly be changed from year to year. In its present form the theory corresponds very well with many known facts and gives us a very vivid picture of affinity and valence. We can use this picture theory with advantage if we keep in mind that it is largely a *theory*.

TABLE GIVING THE USUAL VALENCES OF SOME OF THE MORE COMMON ELEMENTS

(This table is also printed on the page opposite the inside back cover.)

Aluminum	$+3$	Cobalt	$+2$	Nitrogen	$-3, +3, +5$
Antimony	$+3, +5$	Copper	$+1, +2$	Oxygen	-2
Argon	$+0$	Gold	$+1, +3$	Phosphorus	$-3, +3, +5$
Arsenic	$+3, +5, -3$	Hydrogen	$+1$	Potassium	$+1$
Barium	$+2$	Iodine	$-1, +5$	Silicon	$+4$
Bismuth	$+3$	Iron	$+2, +3$	Silver	$+1$
Bromine	-1	Lead	$+2$	Sodium	$+1$
Calcium	$+2$	Magnesium	$+2$	Sulfur	$-2, +4, +6$
Carbon	$+4, -4$	Mercury	$+1, +2$	Tin	$+2, +4$
Chlorine	$-1, +5$	Nickel	$+2$	Zinc	$+2$

CHAPTER SUMMARY IN QUESTION FORM

1. Show by formulas that one atom of each of the elements chlorine, oxygen, nitrogen, and carbon combines with a different number of hydrogen atoms to form compounds.

2. (*a*) One atom of sodium replaces how many atoms of hydrogen in a reaction? (*b*) One atom of zinc replaces how many atoms of hydrogen?

3. Define *valence*, and give examples to illustrate its meaning.

4. What is our standard for valence, and why was it chosen?

5. Give the names of the classes into which elements are divided according to their valences.

6. According to what rule will (*a*) atoms of the same valence combine? (*b*) atoms of different valences?

7. When one element takes the place of another in a reaction, the exchange is between what numbers of the two atoms?

8. Illustrate the difference between molecular formulas and structural formulas by writing each of these formulas for water.

9. (*a*) What do we mean by the term *octet*? (*b*) What elements have complete octets? (*c*) What is the characteristic property of these elements?

10. From the standpoint of atomic structure, of what does chemical action consist?

11. In what two ways may an atom complete an outer orbit?

12. (*a*) Distinguish between electrovalent (or polar) compounds and covalent (or nonpolar) compounds. (*b*) Give an example of each.

13. From the standpoint of our modern views concerning the structure of atoms, to what is the valence of an atom due?

14. (*a*) Explain what is meant by the terms *positive valence* and *negative valence.* (*b*) Give an example of each.

15. (*a*) What is meant by *valence electrons*? (*b*) Where are they located?

16. How does the electron theory account for the fact that some elements have more than one valence?

17. (*a*) What simple methods do we often use to represent the structure of atoms? (*b*) Illustrate these methods by one or more examples.

18. From the standpoint of atomic structure, define the terms (*a*) *oxidation* and (*b*) *reduction.* (*c*) Give an example to illustrate each of these terms.

THOUGHT QUESTIONS

1. How can you tell from the number of electrons in the outer orbit of its atom whether any given element is chemically active or inert?

2. (*a*) What is the valence of copper (see table, p. 207)? (*b*) What is the valence of chlorine? (*c*) Give the formulas of the compounds that you would expect copper to form with chlorine.

3. Give the formulas for the compounds that you would expect each of the following pairs of elements to form: (*a*) iron and chlorine; (*b*) tin and iodine; (*c*) mercury and oxygen; (*d*) magnesium and argon; (*e*) aluminum and oxygen.

4. Give the proportions in which you would expect each of the following pairs of atoms to replace each other: (*a*) chlorine and iodine; (*b*) hydrogen and tin; (*c*) zinc and silver; (*d*) aluminum and hydrogen.

5. Complete and balance the following equations representing reactions between two compounds in which the first element in the one compound exchanges places with the first element in the other:

$$H_2S + HgCl_2 \longrightarrow \qquad BaCl_2 + H_2SO_4 \longrightarrow$$
$$H_2S + BiCl_3 \longrightarrow \qquad Fe_2O_3 + HCl \longrightarrow$$

OPTIONAL EXERCISES

1. Copy Fig. 146 (or a similar one) on a piece of white cardboard; then cut it into sections along the heavy lines. The numerals represent valence. Thus *A* represents one atom of a univalent element; *B*, one atom of a bivalent element; *E*, one atom of a quinquivalent element.

By placing one or more strips of one kind under one or more of another, represent the compound that is formed by the following combinations: *A* and *B*; *A* and *C*; *B* and *C*; *B* and *D*; *B* and *E*.

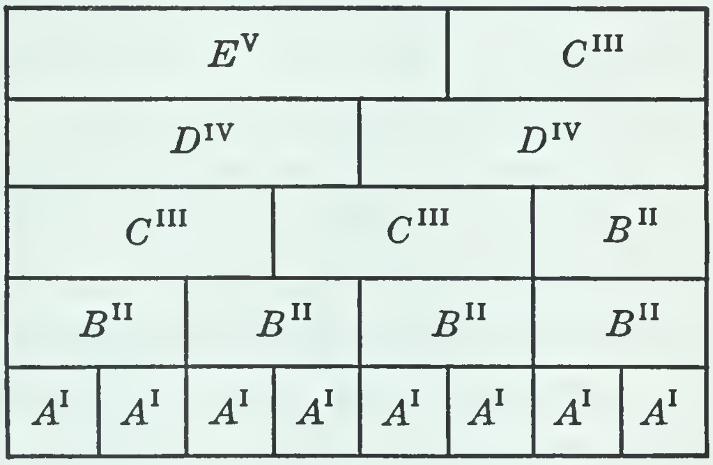


FIG. 146. Exercise in valence

2. Select various compounds so far named or studied that contain but two elements, and show which of the above combinations each represents.

CHAPTER XVIII

Some Problems the Chemist Must Be Able to Solve

Why must the chemist solve problems? The chemist is constantly meeting with problems that he must be able to solve if he is to be successful in his work. For example, suppose you wish to prepare a certain weight (or volume) of oxygen; what weight of potassium chlorate must you heat in order to get the desired results? If you take too little, you will not get enough oxygen; if you take too much, you will waste some of the potassium chlorate.

Or suppose you wish to get enough hydrogen to fill a balloon of a certain volume. What weight of sulfuric acid will be required, and what weight of zinc or iron to set free the hydrogen from the acid?

The industrial chemist, making hundreds of tons of soap or glass, must know not only what materials to use but the weight of each needed to make the desired amount. Unless he can accurately calculate these quantities, he is not a chemist and will soon lose his job.

Formulas and equations, the keys to the solution of most problems. In order to solve most of his problems, the chemist must know the formulas of the compounds with which he is dealing, as well as the equations for the reactions that take place between these compounds.

The formulas show what elements are in a compound, and the relative weights of each. The equations are accurate statements in chemical symbols of the relative weights of all materials taking part in a reaction and formed in it. When, by experiment, we have found such an equation for a reaction, we can use it to calculate (1) the actual weights of materials used up in the reaction; (2) the yields that are possible from given weights of materials; (3) the weights of materials required to make the weight of the product we want to get.

Getting ready for problems. In learning to use equations for the solution of problems, it is best for the beginner to follow a definite plan until, through experience, he can clearly see the steps he can safely omit. The steps are these:

1. Write the correct formula for each of the substances taking part in the reaction, and balance the equation.
2. Under each formula write the formula (gram-molecular) weight times the coefficient (if any) before the formula.
3. Above its formula write the weight of the substance whose weight is given you; and write x above the formula of the substance whose weight you are asked to calculate.
4. Solve for x.

The following problems illustrate this plan of work.

Problem 1. How many grams of copper oxide will be formed by heating 60 g of copper in air?

$$\text{Copper} + \text{oxygen} \longrightarrow \text{copper oxide}$$

$$\mathrm{Cu} + \mathrm{O_2} \longrightarrow \mathrm{CuO}$$

1. $$2\,\mathrm{Cu} + \mathrm{O_2} \longrightarrow 2\,\mathrm{CuO}$$

2 and 3. $$\underset{2\times 63.57}{\overset{60\text{ g}}{2\,\mathrm{Cu}}} + \underset{2\times 16}{\mathrm{O_2}} \longrightarrow \underset{2(63.57+16)}{\overset{x}{2\,\mathrm{CuO}}}$$

4. $$\frac{60\text{ g}}{127.14} = \frac{x}{159.14}$$

By clearing of fractions:

$$127.14\,x = 159.14 \times 60\text{ g}; \quad \text{or} \quad x = 75.1\text{ g}$$

Problem 2. How many grams of potassium chlorate will be needed to yield 100 g of oxygen?

$$\text{Potassium chlorate} \longrightarrow \text{potassium chloride} + \text{oxygen}$$

$$\mathrm{KClO_3} \longrightarrow \mathrm{KCl} + \mathrm{O_2}$$

1. $$2\,\mathrm{KClO_3} \longrightarrow 2\,\mathrm{KCl} + 3\,\mathrm{O_2}$$

2 and 3. $$\underset{2(39.1+35.46+3\times 16)}{\overset{x}{2\,\mathrm{KClO_3}}} \longrightarrow \underset{2(39.1+35.46)}{2\,\mathrm{KCl}} + \underset{3(16\times 2)}{\overset{100\text{ g}}{3\,\mathrm{O_2}}}$$

4. $$\frac{x}{245.12} = \frac{100\text{ g}}{96}$$

By clearing of fractions:

$$96\,x = 245.12 \times 100\text{ g}; \quad \text{or} \quad x = 255.3\text{ g}$$

Units other than the gram. In these problems the *gram* was used as the unit of weight, as it is the unit ordinarily used. But since atomic and molecular weights are simply *relative* weights, we may use any other unit of weight (such as the kilogram, pound, or ton) provided we are consistent and use the same unit throughout the problem. For example, suppose we change Problem 1 above to read as follows: How many pounds of copper oxide will be formed by heating 60 pounds of copper in the air? The problem would be solved in exactly the same way, using the identical figures; but the answer would be, not 75.1 g, but 75.1 lb.

Problems that have to do with volumes of gases. Often we must be able to calculate the *weight* of material needed to obtain a certain *volume* of a gas; or what *volume* of a gas will be given off in a certain reaction. In all such problems we must change the *volume* of a gas into its *weight* (or vice versa); for atomic weights are used to calculate *weights*, not volumes. Two problems will show how this is done.

Problem 3. Suppose you wish to prepare 100 liters of oxygen. How many grams of potassium chlorate will be required?

First find the weight of 100 liters of oxygen. One liter of oxygen weighs 1.429 g; so 100 liters will weigh 142.9 g. We can now state the problem by weight as follows: What weight of potassium chlorate will be required for the preparation of 142.9 g of oxygen? We then proceed as in Problem 2. The equation (steps 2 and 3) is

$$2\,\underset{245.12}{\overset{x}{KClO_3}} \longrightarrow 2\,KCl + 3\,\underset{96}{\overset{142.9\text{ g}}{O_2}}$$

$$\frac{x}{245.12} = \frac{142.9}{96}$$

$$96\,x = 245.12 \times 142.9$$

$$x = 364.8 \text{ g of potassium chlorate required}$$

Problem 4. What volume of oxygen can I get by heating 100 g of potassium chlorate?

First find the weight of the oxygen evolved, as in Problem 2. The equation (steps 2 and 3) is as follows:

$$2\,\underset{245.12}{\overset{100\text{ g}}{KClO_3}} \longrightarrow 2\,KCl + 3\,\underset{96}{\overset{x}{O_2}}$$

$$\frac{100}{245.12} = \frac{x}{96}$$

$$245.12\,x = 96 \times 100$$

$$x = 39.16 \text{ g of oxygen gas}$$

But 1 liter of oxygen weighs 1.429 g. In 39.16 g there will be 39.16 ÷ 1.429, or 27.4 liters of oxygen.

Avogadro's law used in the solution of problems. By making use of Avogadro's law we can easily solve a number of problems that have to do with the volume relations of gases. The following will illustrate the kind of problems that can be solved in this way, as well as the way to solve them.

1. Knowing the formula of a gaseous element or compound, calculate the *approximate* weight of 1 liter of the gas.

Example. The formula of carbon dioxide is CO_2. Calculate the approximate weight of 1 liter of this gas.

Since the formula is CO_2, its molecular weight must be equal to 12 (atomic weight of carbon) $+ 2 \times 16$ (atomic weight of oxygen), or 44. But we have seen that the number which represents the molecular weight of a gaseous element or compound also equals the weight in grams of 22.4 liters of the gas. So 22.4 liters of carbon dioxide weighs 44 g, and 1 liter weighs $44 \div 22.4$, or 1.9643 g.

The steps in solving problems of this type are (1) to calculate the molecular weight of the gas from its formula, and (2) to divide the number representing its molecular weight by 22.4.

The results obtained by this method are only approximate. Thus we obtained the value 1.9643 g as the weight of 1 liter of carbon dioxide. The real value is 1.9768 (see table facing back cover). The reason why the results are only approximate is that many gases do not act strictly in accordance with the gas laws.

2. Knowing the equation for the reaction that takes place between two gases, calculate the relative volumes of the gases and of any gaseous product.

Example. Suppose you burn 100 liters of carbon monoxide. (*a*) How many liters of oxygen will be needed to burn it, and (*b*) how many liters of carbon dioxide will be formed?

The equation for the reaction is

$$2\,CO + O_2 \longrightarrow 2\,CO_2$$

In other words, 2 molecules of carbon monoxide combine with 1 molecule of oxygen to form 2 molecules of carbon dioxide. But Avogadro's law tells us that equal volumes of gases correspond to equal numbers of molecules. So we may substitute the word *volume* for the word *molecule* in reading the above equation and say that 2 volumes of carbon monoxide combine with 1 volume of oxygen to form 2 volumes of carbon dioxide. It follows, then, that 100 liters of carbon monoxide combine with 50 liters of oxygen to form 100 liters of carbon dioxide. These facts may be represented as follows:

$$\begin{array}{lrcl} & 2\,CO + O_2 & \longrightarrow & 2\,CO_2 \\ & \text{2 molecules} + \text{1 molecule} & \longrightarrow & \text{2 molecules} \\ & \text{2 volumes} + \text{1 volume} & \longrightarrow & \text{2 volumes} \\ \text{or} & \text{100 liters} + \text{50 liters} & \longrightarrow & \text{100 liters} \end{array}$$

The steps in solving problems of this type are as follows: (1) write the equation for the reaction; (2) note the relation between the numbers of molecules of the gases taking part in the reaction. This relation is the same as the relation between the volumes of the gases.

PROBLEMS

(All may be solved or selections may be made.)

Note. In showing how problems are solved (pp. 210–214), accurate atomic weights were used. To save time spent in merely multiplying and dividing large numbers, many teachers prefer to use the nearest whole number as the atomic weight of an element. A table of the whole numbers to be used will be found in the table opposite the back cover of the book.

The volumes of all gases are to be regarded as measured under standard conditions. The weight of 1 liter of each of the common gaseous elements and compounds, measured under standard conditions, is given in the table opposite the back cover of the book.

1. Calculate the molecular weight of each of the following compounds from its formula: potassium chlorate ($KClO_3$); mercuric oxide (HgO); hydrogen sulfate (H_2SO_4); potassium chloride (KCl); calcium carbonate ($CaCO_3$).

2. (*a*) Calculate the volume of 100 g of oxygen; (*b*) of 100 g of hydrogen; (*c*) of 100 g of carbon dioxide.

3. (*a*) Write the equation for the decomposition of water by electrolysis. Suppose that 10 g of water is decomposed in this way. (*b*) What weights of hydrogen and of oxygen will be set free? (*c*) Calculate the volume of each of the gases set free.

4. A student heated 10 g of potassium chlorate until all its oxygen was set free. (*a*) What weight of oxygen did he get? (*b*) What volume?

5. Suppose that the student referred to in problem 4 had heated 10 g of mercuric oxide. (*a*) What weight of oxygen would he have obtained? (*b*) What volume?

6. Suppose you were to heat 40 g of potassium chlorate in a flask until all the oxygen was given off. (*a*) What compound would remain in the flask? (*b*) Calculate its weight.

7. A student prepared oxygen by heating 25 g of potassium chlorate mixed with 3 g of manganese dioxide (see page 84). (*a*) What weight of oxygen was obtained? (*b*) What volume? (*c*) What compounds remained in the flask? (*d*) Calculate the weight of each.

8. Suppose you wished to prepare 20 liters of oxygen. What weight of potassium chlorate would be required?

9. Suppose you wished to prepare 20 g of hydrogen by the action of zinc on sulfuric acid. What weight of zinc and what weight of hydrogen sulfate would be required?

10. I wish to get enough hydrogen to inflate a small balloon that holds 100 liters of the gas. (*a*) What will this volume of hydrogen weigh? (*b*) Calculate the weights of zinc and hydrogen sulfate that will be needed to prepare the necessary hydrogen.

11. 100 g of zinc was added to an amount of sulfuric acid that contained 98 g of hydrogen sulfate. (*a*) What volume of hydrogen was given off? (*b*) What substances remained in the flask?

12. (*a*) From the formula CO calculate the approximate weight of 1 liter of carbon monoxide. (*b*) Compare your result with the weight as given in the Appendix. (*c*) If the results differ, which is the more trustworthy?

13. (*a*) What weight of carbon dioxide is formed in the combustion of 10 g of carbon? (*b*) What volume?

14. Write the equation for getting carbon dioxide by the action of hydrochloric acid on calcium carbonate (marble) (p. 149). (*a*) What weight of carbon dioxide can be obtained from 100 g of calcium carbonate by this method? (*b*) What volume will this weight of the gas occupy?

15. 1 g of coal, when burned, gave 2.9 g of carbon dioxide. (*a*) Calculate the weight of carbon present in the 2.9 g of the dioxide. (*b*) Calculate the percentage of carbon present in the sample of coal burned.

16. Methane (CH_4) is the chief constituent of natural gas. It burns in accordance with the following equation:

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O$$

(*a*) How many cubic feet of oxygen would be needed to burn 1000 cu ft of the gas? (*b*) How many cubic feet of carbon dioxide would be formed? (Solve by Avogadro's law.)

UNIT READINGS

BEERY. *Stuff.* [Pages 399–409 discuss the structure of the atom in a simple way.]

CUNNINGHAM. *Adventures in Science.* [Read pages 164–178, "The Method of Scientific Investigation."]

DARROW. *The Story of Chemistry.* [Chapter III, "Atoms, Electrons, and Protons," contains 71 pages of information, most of which can be understood by students beginning the study of chemistry.]

FOSTER. *The Romance of Chemistry.* [Chapter III, "Electrons, Atoms, and Molecules," is brief but worth reading.]

FRENCH. *The Drama of Chemistry.* [Chapter VI gives a good discussion of the structure of atoms and molecules.]

JAFFE. *Chemical Calculations.* [Students who expect to go far in chemistry will be interested in this little book. It gives the solution of type problems and also contains many problems arranged progressively according to lesson assignments.]

JAFFE. *Crucibles.* [Chapter XIV gives a brief but very interesting account of J. J. Thomson, the great English scientist who discovered the electron.]

KENDALL. *At Home among the Atoms.* [A popular treatise on the subject.]

NOYES AND NOYES. *Modern Alchemy.* [Chapter II, "Atomic Structure," is of interest to the student who wishes to go into the subject somewhat in detail.]

The Science Leaflet. [The student will find much of interest about the structure of atoms in No. 3 of recent volumes of this publication.]

Unit Five. Three Related Groups of Compounds: Acids, Bases, and Salts

HAVE you ever stopped to think what you would do if you could no longer get something you use all the time? What should you do without salt? Men have prized it so highly they have used it in place of coined money. Nations have waged wars to get possession of salt mines.

How could we get along if we had no lye and, as a result, no soap? How could we manage without sulfuric acid for our batteries, lime for our mortars, soda for making baking powder, soda ash for making glass?

Now each of these necessities belongs to one of three great classes of chemical compounds called, respectively, acids, bases, and salts. Before we attempt to study the special properties of any large number of such compounds, it will be a great help to have clearly in mind just what is meant by the terms *acid*, *base*, and *salt*. Why do we call this compound an acid and that one a base or a salt? How do these compounds act on each other? Why do their solutions in water always conduct the electric current, while solutions of no other kind do? Why does the electric current deposit some metals from solutions of their salts (plate them out) and not others?

This unit will center about the nature of the three great classes acids, bases, and salts, and the theories that have been imagined to account for some of their peculiarities.

CHAPTER XIX

Chlorine; Hydrogen Chloride; Hydrochloric Acid

[An Important Element and Two of Its Compounds]

Chemical pioneers. At the time the American pioneers were pushing over the Eastern mountains into the lands of Ohio and Kentucky, the pioneers of real chemistry were doing great things in Europe. We have met several of them — Priestley, Cavendish, and Lavoisier. In this chapter we meet another. While, in England, Priestley was bringing to light a whole group of new gases, the great Scheele (Fig. 147) was making equally important experiments in Sweden.

When still not much more than a boy, Scheele was apprenticed to a pharmacist and so became acquainted with the chemical substances of the time. He soon began to experiment with them and in his brief lifetime made many important discoveries. In the same year (1774) in which Priestley heated mercuric oxide and got oxygen, Scheele obtained a strange greenish-yellow gas which much later was named *chlorine,* from a Greek word meaning "pale green."

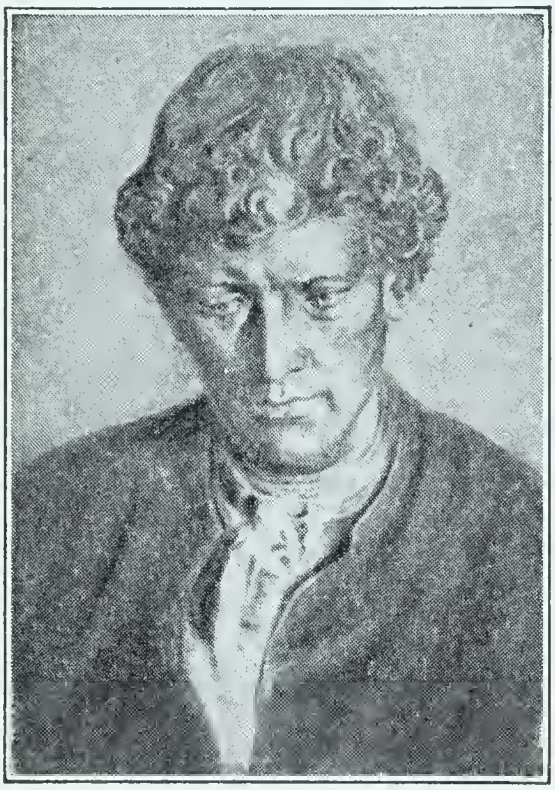


FIG. 147. Karl Wilhelm Scheele (1742-1786)

This Swedish chemist was one of the greatest experimenters of his century. He discovered oxygen independently of Priestley, as well as the elements chlorine, tungsten, and molybdenum. He was one of the ablest as well as one of the latest defenders of the phlogiston theory of combustion

I. CHLORINE

Although very useful, chlorine is a dangerous element. Nearly all the poison gases used in the World War were either chlorine or some of its compounds (Fig. 151). So while working with chlorine one must be very careful *not to breathe the gas.* In even very small quantities in air it irritates the throat and lungs, and a full, deep breath of it might be fatal.

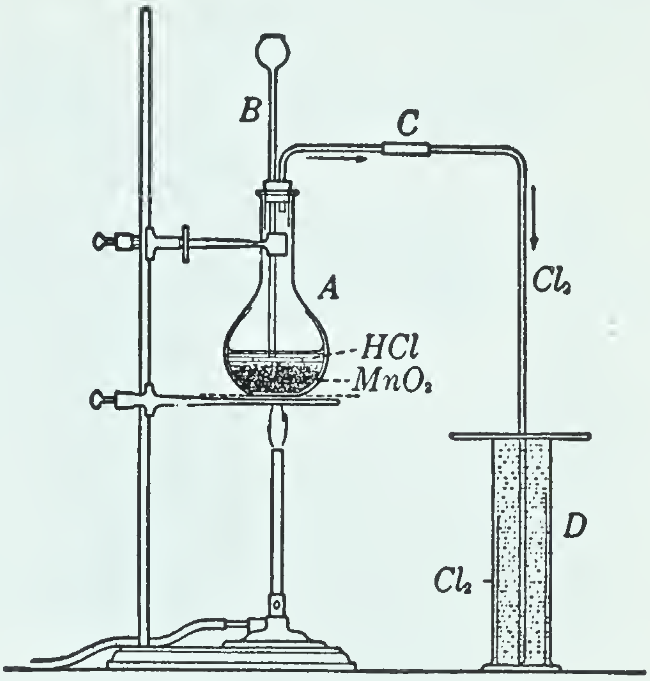


Fig. 148. The preparation of chlorine

Manganese dioxide is placed in the flask *A*, and hydrochloric acid is added through the funnel tube *B*. Chlorine gas escapes through the tube *C*. Since it is much heavier than air, it is delivered at the bottom of the bottle *D*, and fills the bottle by displacing the air upward

Chlorine a widespread element. Unless we have studied chemistry, we are not likely to know much about chlorine, though its compounds occur in our bodies, in our foods, in the soil, in all natural waters, and in many rocks. Its most abundant compounds are those in which chlorine is combined with a metal, forming a *chloride.* Great beds of sodium chloride (or common salt) are found in many parts of the world. Most of the compounds in salt waters are chlorides, chiefly sodium chloride ($NaCl$), potassium chloride (KCl), and magnesium chloride ($MgCl_2$). Sodium chloride is by far the most abundant of these, and it is from it that chlorine and all its compounds are made.

How we get free chlorine. No free chlorine is found in nature; so it has to be got from its compounds. Scheele got it by the action of hydrochloric acid (HCl) on manganese dioxide (MnO_2), the black mineral we met in preparing oxygen (p. 84); and we still use this method in the laboratory. When these two compounds are warmed together (Fig. 148), chloride of manganese ($MnCl_2$) and water are formed, and chlorine is set free. The equation for the reaction is as follows:

$$MnO_2 + 4\,HCl \longrightarrow MnCl_2 + 2\,H_2O + Cl_2\uparrow$$

Instead of the hydrochloric acid in this reaction it does just as well to use a mixture of sodium chloride and sulfuric acid, since these two compounds react together to form hydrochloric acid. In this case the complete reaction is expressed by the equation

$$MnO_2 + 2\,NaCl + 2\,H_2SO_4 \longrightarrow Na_2SO_4 + MnSO_4 + 2\,H_2O + Cl_2\uparrow$$

The commercial method for getting chlorine. While the method just described for getting chlorine is easy to carry out, and is well suited to the laboratory, where only small quantities are wanted, it is rather expensive. In large quantities for commercial purposes, chlorine is always set free by the electrolysis of a solution of sodium chloride. The electrolysis results not only in the formation of chlorine, but also of hydrogen, and sodium hydroxide (NaOH). The chlorine is liberated at the anode (B^+) and the hydrogen at the cathode (A^-), as shown in Fig. 149. The sodium hydroxide remains in solution and may be recovered by evaporation. The mechanism of the reactions involved is somewhat complicated and will be explained later in the chapter on ionization. For the present it is only necessary to remember that this method is the one used in the commercial preparation of chlorine.

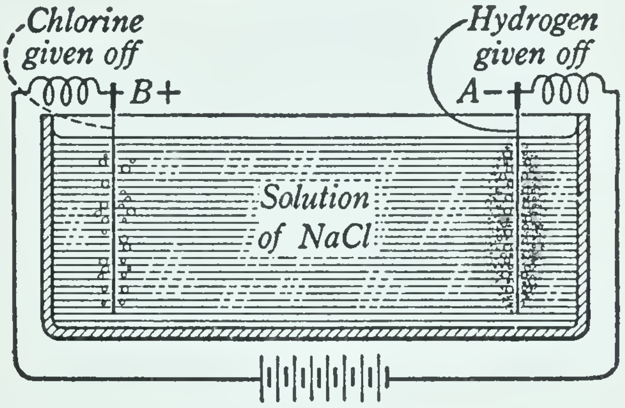


Fig. 149. Illustrating the electrolysis of a solution of sodium chloride (NaCl)

While Fig. 149 shows in a simple way the principles involved in the electrolysis of sodium chloride, the actual apparatus used is rather complicated. This is because it is necessary to prevent the chlorine from coming into contact with the sodium hydroxide formed; for these two substances act on each other.

Many different forms of electrolytic apparatus have been invented for getting chlorine, each one called a *cell.* One of the most used cells, named, from its inventor, the *Vorce cell,* is shown (in cross section) in Figs. 150 and 152.

The chlorine set free in the electrolysis either is used up in the plant where it is made or else is compressed in strong steel cylinders (Fig. 154), loaded on cars, and shipped in this form to some place where it is needed (Fig. 153). Sometimes it is passed into slaked lime, making the solid called *chloride of lime* or *bleaching powder* (p. 343), which can be shipped easily and from which the chlorine can be recovered as needed.

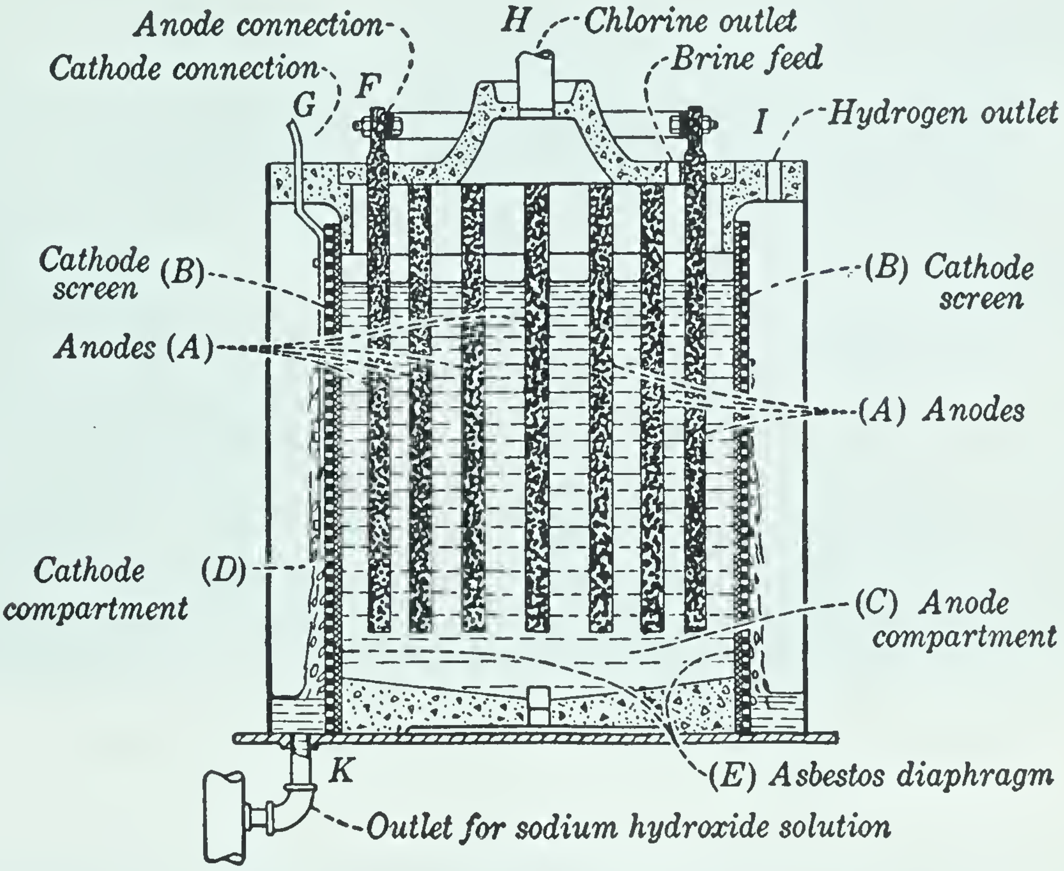

Anode connection
Cathode connection
G
F
H
Chlorine outlet
Brine feed
I
Hydrogen outlet
Cathode screen (B)
(B) Cathode screen
Anodes (A)
(A) Anodes
Cathode compartment (D)
(C) Anode compartment
K
(E) Asbestos diaphragm
Outlet for sodium hydroxide solution

Fig. 150. The Vorce cell for producing chlorine

The salt brine is placed in a large cylindrical container and renewed from time to time through the brine feed. A number of graphite anodes A are dipped into the brine. The cathode of wire screening B surrounds the group of anodes in the form of a hollow cylinder, and is separated from the electrolyte by an asbestos diaphragm E to prevent mechanical stirring of the liquid. Hydrogen is evolved at the cathode and escapes through the hydrogen outlet I. Chlorine is evolved at the anode surfaces, collects under the domelike top, and escapes through the chlorine outlet H. The sodium hydroxide formed in the electrolysis is drawn off at the bottom K of the cell

In preparing chlorine by this method the chief item of expense is the cost of the electric current. For this reason a great center for preparing chlorine is at Niagara Falls, where water power is used for generating the current at a low cost. The electrolytic method has the added advantage that the hydrogen and sodium hydroxide formed in the process along with the chlorine have many commercial uses.

Some physical properties of chlorine. Like oxygen and hydrogen, chlorine is a gas, but it differs from them in many

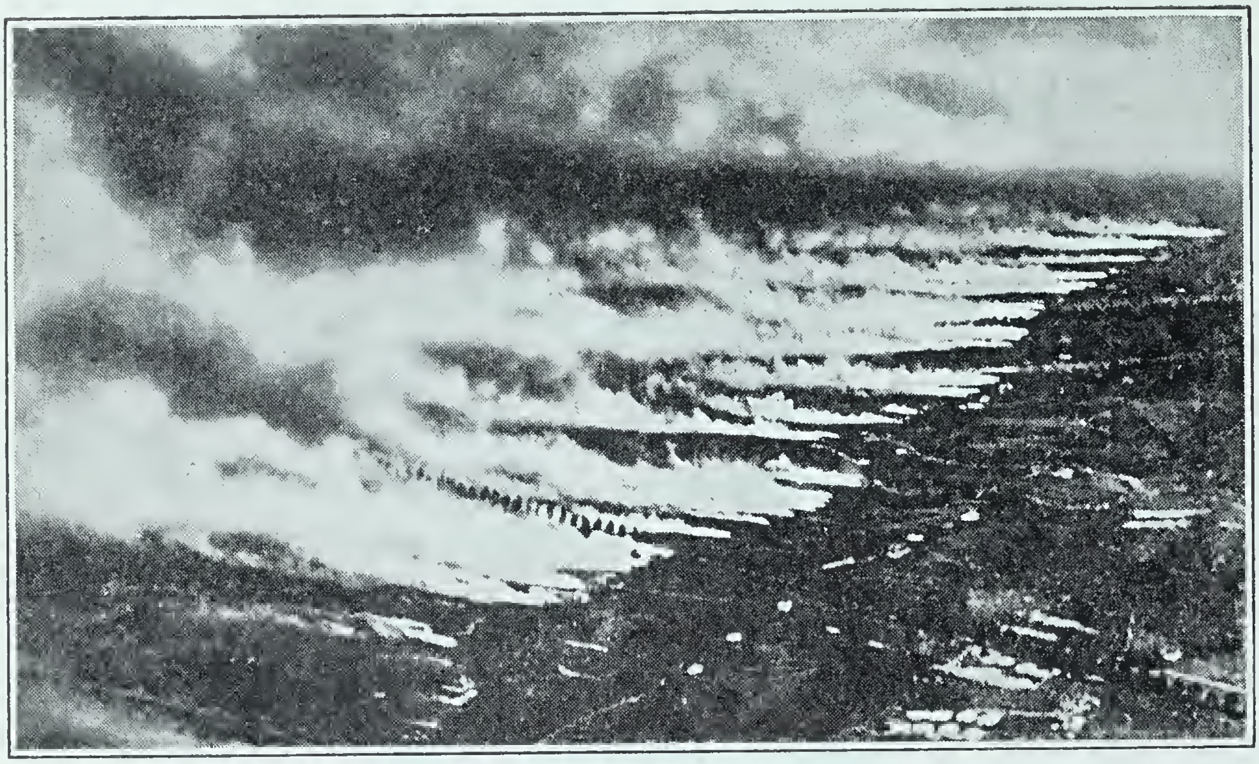


Fig. 151. Making a gas attack in Flanders during the World War

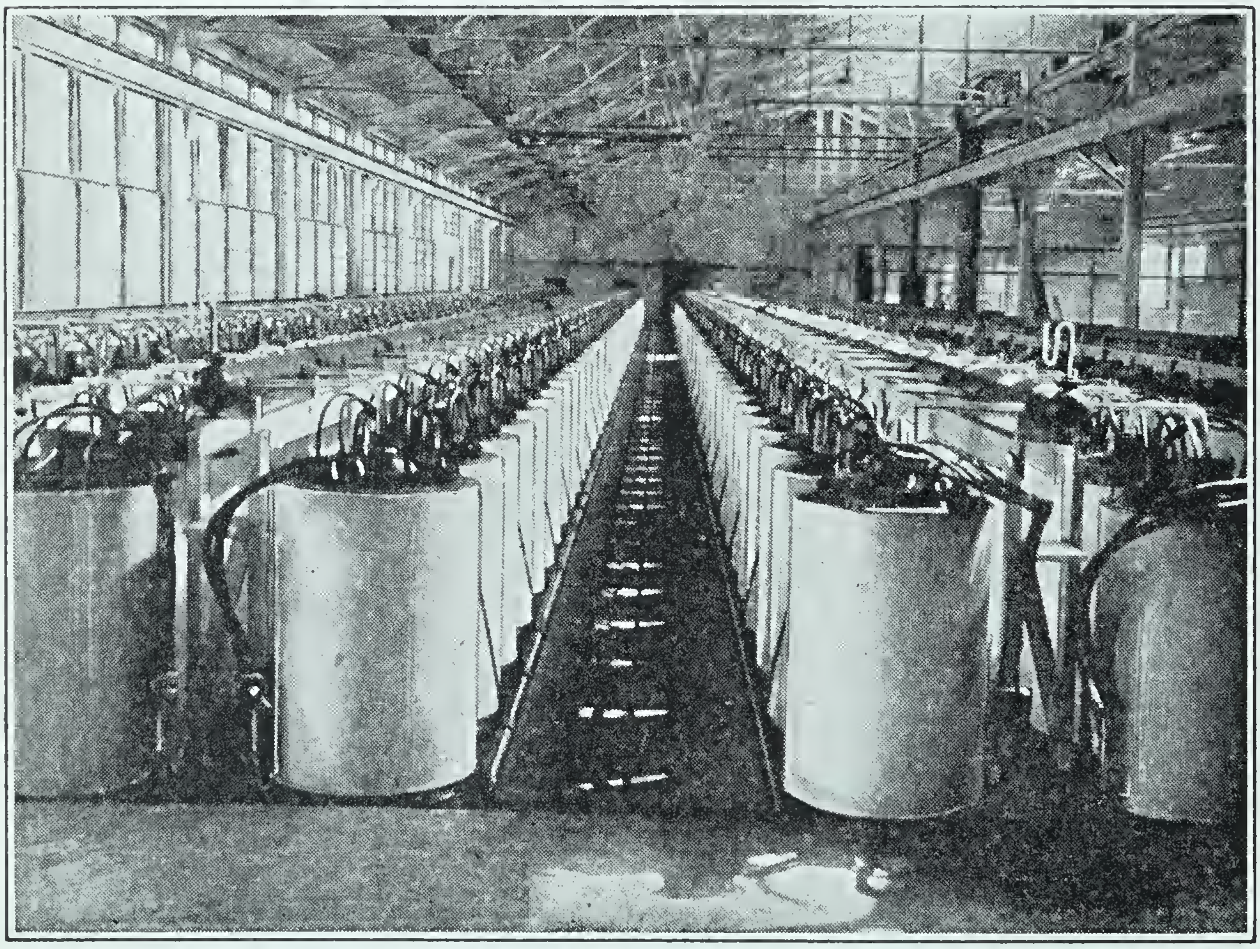


Fig. 152. A room filled with rows of Vorce cells

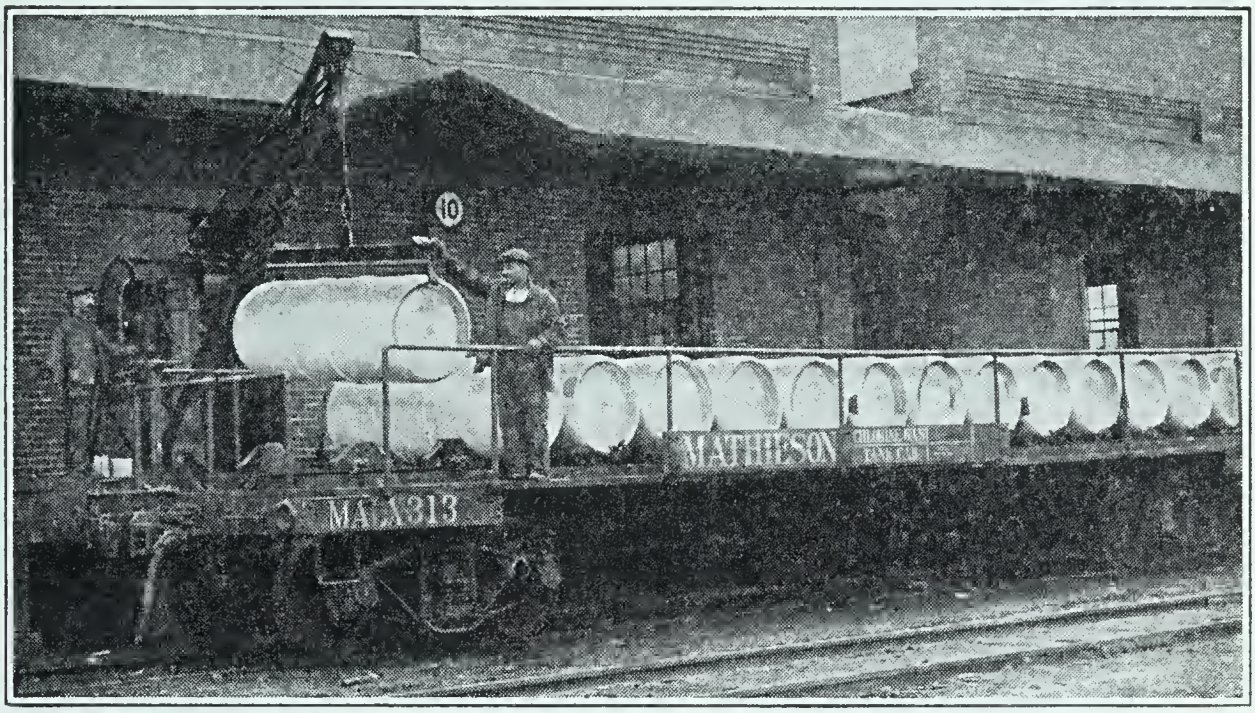

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Fig. 153. Shipping a carload of one-ton containers filled with liquid chlorine

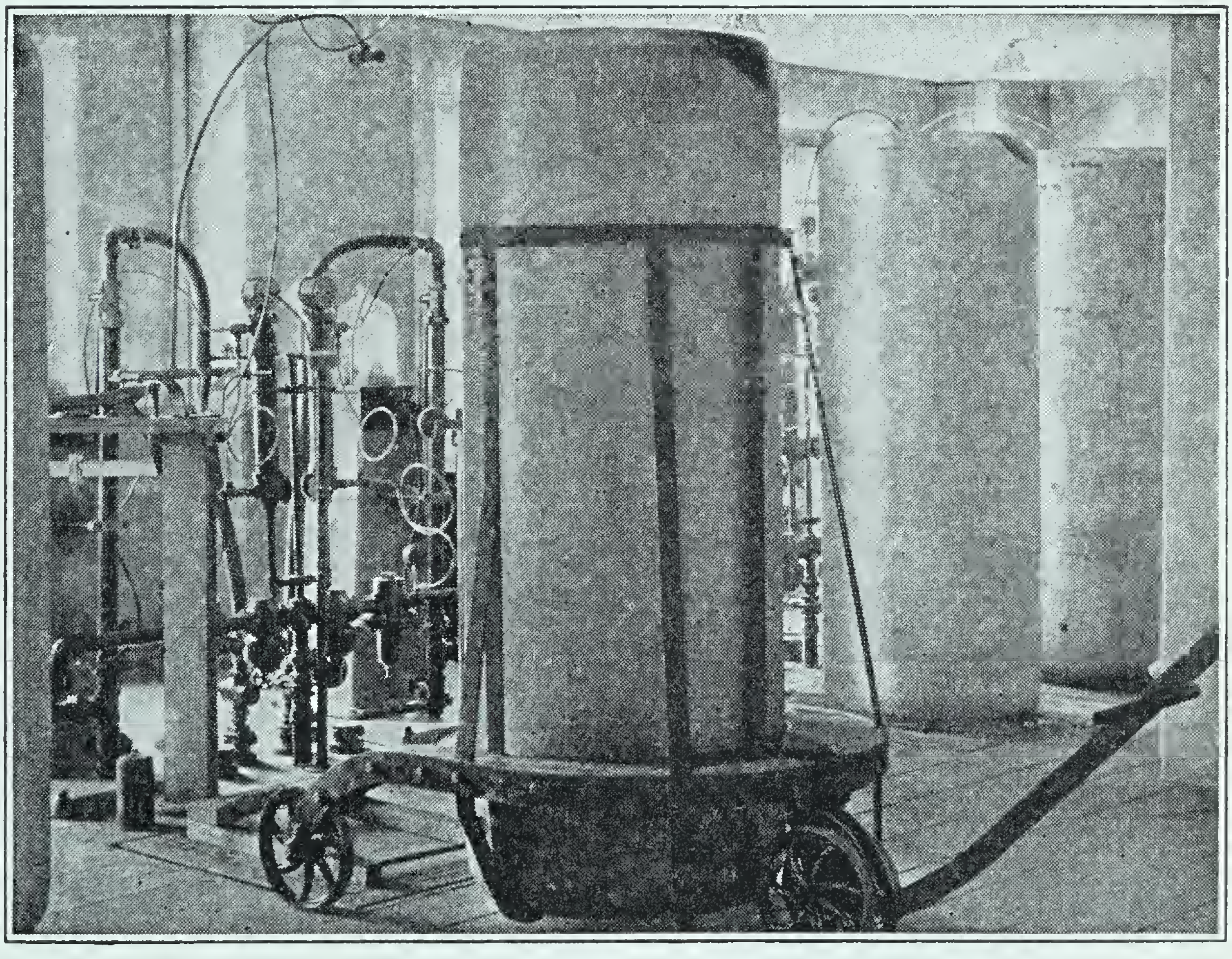


Fig. 154. Filling one-ton containers with liquid chlorine

ways. It has a greenish-yellow color, and it is somewhat soluble in water, 1 volume of water dissolving about 2.5 volumes of chlorine under ordinary laboratory conditions. It is much heavier than hydrogen or oxygen, and is about 2.5 times as heavy as air.

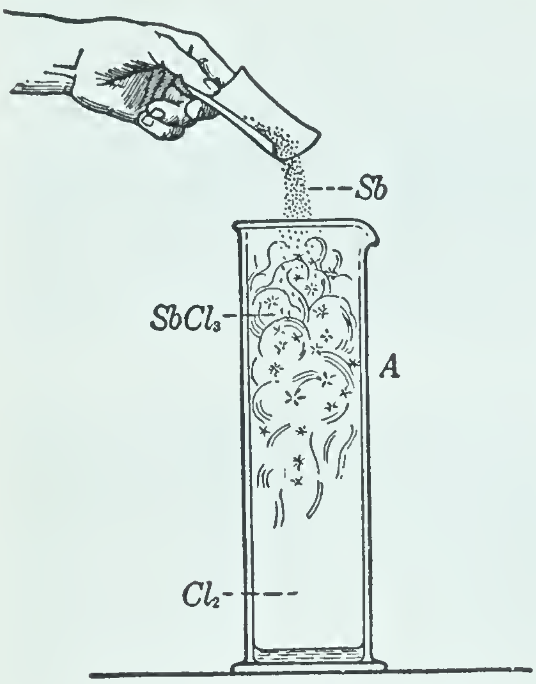


Fig. 155. Powdered antimony burning in chlorine

Chlorine is rather easily condensed to a liquid. At ordinary temperatures (18°) it is liquefied by a pressure of 16.5 atmospheres. On any summer day commercial chlorine, compressed in steel cylinders (or tank cars) for shipment, is at a much higher temperature than this; so it is evident that the chlorine in these cylinders exerts a great pressure, though most of it is in a liquid state.

How chlorine acts chemically. Chlorine is one of the most active of all the elements. It combines with all the metals, especially if they are hot, forming *chlorides*. For example, a strip of hot copper foil dropped into a jar of chlorine burns brilliantly, forming chloride of copper ($CuCl_2$). Iron or antimony or arsenic in the form of a fine powder burns almost like a flashlight when dropped into an atmosphere of chlorine (Fig. 155), forming the corresponding chlorides.

Chlorine has an especially great affinity for hydrogen, the two uniting to form the gas called hydrogen chloride (HCl). For example, a jet of hydrogen burning in air will continue to burn when lowered into a jar of chlorine, giving a somewhat luminous flame (Fig. 156). The two gases may be mixed in the dark without danger; but if an electric spark is passed through the mixture, or if bright sunlight strikes it an instant, a violent explosion takes place as the two gases combine.

Not only will chlorine combine with free hydrogen; it will take the hydrogen away from many of its compounds. A solution of chlorine in water will keep its strength for some time if kept in the dark, but in the sunlight the chlorine slowly succeeds in getting possession of the hydrogen of the water, forming hydrogen chloride and crowding out the oxygen (Fig. 157). It is this property of chlorine that makes it so useful as a bleaching agent.

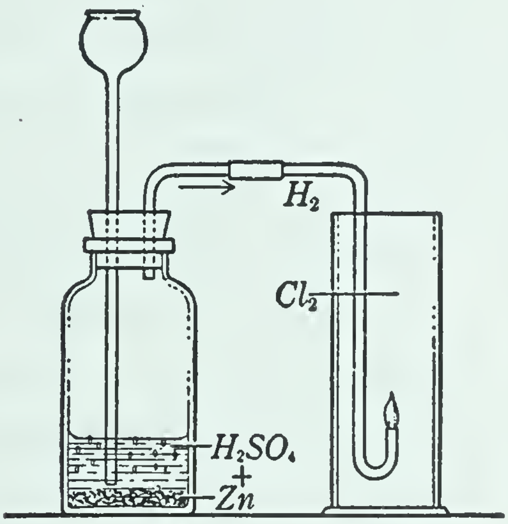


FIG. 156. Burning a jet of hydrogen in chlorine

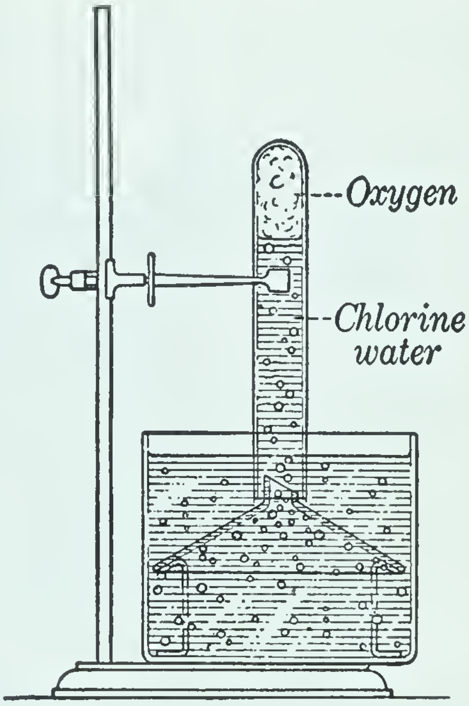


FIG. 157. Action of chlorine on water in strong sunlight

Valence of chlorine. It will be recalled that chlorine has a valence of − 1. Its atom has seven electrons in its outer valence orbit (Fig. 158), and has a strong tendency to capture one additional electron. For this reason we should expect chlorine to combine with hydrogen and with the metals having small positive valences, and this is found to be the fact.

Uses of chlorine. Chlorine has many uses: (1) as a bleaching agent, (2) as a disinfectant, (3) in preparing many carbon compounds. Hundreds of tons of chlorine are produced daily for these uses.

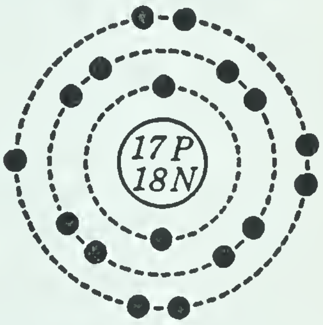


FIG. 158. Structure of the chlorine atom

1. ***Use as a bleaching agent.*** The greatest use of chlorine is as a bleaching agent. The process called bleaching is an important one in many industries. The various kinds of fabrics woven from vegetable fibers, such as flax and cotton, are always more or less colored in the natural state, and bleaching is necessary if a white fabric is wanted. This was formerly done by spreading

the cloth on plots of grass in the air and sunlight, but the bleaching was very slow. The same results are now reached in a much shorter time by the use of chlorine. Most of our paper is made from wood pulp, which must be bleached to form a white paper. The greatest single use of chlorine is in the bleaching of this wood pulp.

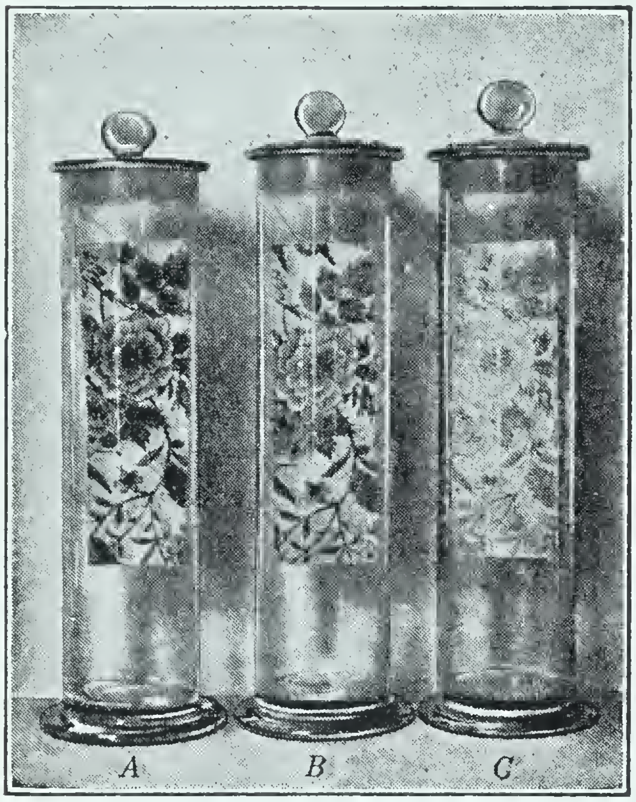


FIG. 159. Bleaching with chlorine

The jars *A*, *B*, *C* were filled with dry chlorine. The cloth in *A* was dry; in *B*, slightly moist; in *C*, thoroughly wet

2. ***Use as a disinfectant.*** In the chapter on water we saw that disease-producing bacteria in the water supply of our cities are a constant source of danger to health. Practically every city must purify its water supply, and chlorine is almost always used in the process. It is estimated that three billion gallons of water, or the equivalent of the volume of water that flows over Niagara Falls in forty-four seconds, is purified daily by the use of liquid chlorine. In this way typhoid fever has been greatly reduced (Fig. 83).

Why is chlorine a bleaching agent? If strips of bright-colored cloth or some highly colored flowers are placed in *dry* chlorine, we can usually see little change in their color. If the cloth or flowers are first *moistened* with water, the color rapidly disappears (Fig. 159). Evidently the moisture as well as the chlorine is necessary for bleaching. Experiment shows that the chlorine sets the oxygen free from the water (Fig. 157), and the oxygen so liberated oxidizes the color substance (dye), changing it into a colorless compound. From this explanation it is clear that chlorine will bleach only such substances as are changed into colorless compounds by oxidation. It has no action on carbon, and so does not affect printer's ink made from carbon black. It must not be used for bleaching silk or wool, because it injures the fabric.

Nascent state. It is a striking fact that while oxygen is being set free from water by chlorine, it is much more active than ordinary oxygen. It bleaches substances quickly; yet in pure air or oxygen the same substances remain unchanged or bleach very slowly. Many elements other than oxygen have this increased activity just as they are being set free from their compounds.

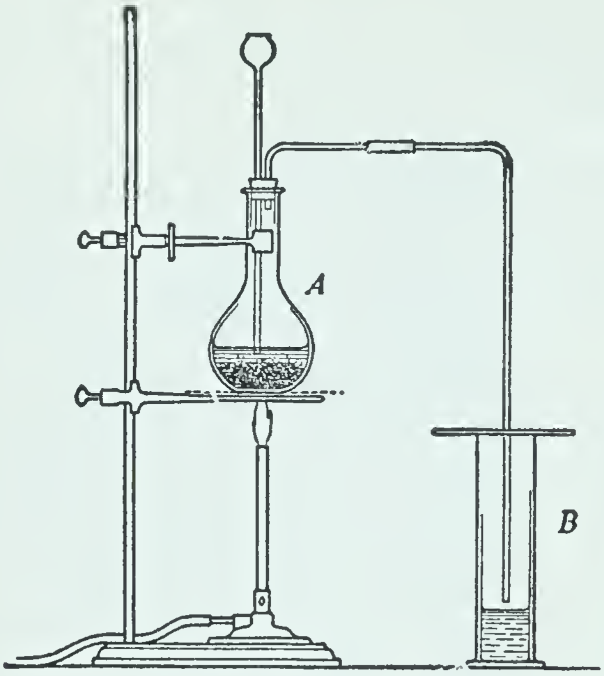
We explain this fact by saying that for an instant the element set free is in the form of *single atoms* (p. 33), which are much more active than they are after they have had time to combine into molecules. At the instant of liberation the atoms are said to be in the *nascent state*, the word *nascent* coming from a Latin word meaning "being born." It is *nascent* oxygen that does the bleaching.

Use of chlorine compounds in medicine. While chlorine itself is a poisonous element, many of its compounds are of great use in medicine. For example, chloroform ($CHCl_3$) and ethyl chloride (C_2H_5Cl) are common anesthetics. Carbon tetrachloride (CCl_4) is used in fighting the hookworm disease. Potassium chlorate, which we used in preparing oxygen, and the chlorides of many of the metals, such as mercurous chloride (calomel, $HgCl$), and ferric chloride ($FeCl_3$), are all common medicines.

II. HYDROGEN CHLORIDE; HYDROCHLORIC ACID

Hydrogen chloride (HCl). When hydrogen and chlorine combine, a colorless gas is formed, called *hydrogen chloride.* This is a very important compound; for its solution in water is *hydrochloric acid*, which has many commercial uses. The pure hydrogen chloride is 1.26 times as heavy as air. When inhaled it has an irritating, choking effect. It is very soluble in water. One volume of water, under standard conditions, dissolves a little more than 500 volumes of the gas. When exposed to moist air, hydrogen chloride gas attracts moisture, which condenses into minute droplets, forming visible clouds or fumes.

How we get hydrogen chloride. Hydrogen chloride can be got by burning hydrogen in chlorine (Fig. 156). It is much



The sodium chloride is placed in the flask *A*, and the flask is connected with stopper and tubes as shown in the figure. Sulfuric acid is added through the funnel tube, and the mixture is gently heated. The hydrogen chloride formed escapes through the exit tube and can be collected by displacement of air as in the case of chlorine (Fig. 148). To prepare a solution of the gas, the end of the exit tube is fixed *just above* the level of some water in the cylinder *B*. The gas, being very soluble, dissolves in the water as fast as it escapes from the tube

Fig. 160. The preparation of a solution of hydrogen chloride

cheaper and much easier to get it by the action of sulfuric acid on sodium chloride (Fig. 160). The two react as follows:

$$2\,NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HCl\uparrow$$

Hydrochloric acid. To prepare hydrogen chloride on a commercial scale the sodium chloride and sulfuric acid are heated together in large furnaces (Fig. 161). The hydrogen chloride formed is dissolved in water, forming the *hydrochloric acid* of commerce. Made in this way it always contains impurities, and the impure product is often called *muriatic acid.* When desired, the pure acid is obtained from this product by removing the impurities.

The properties and chemical conduct of hydrochloric acid. Pure hydrochloric acid is a colorless liquid of great importance, the density (p. 120) of which increases with the amount of hydrogen chloride dissolved. The ordinary concentrated acid used in our laboratories has a density of about 1.19 and contains from 38 to 39 per cent by weight of hydrogen chloride.

It is interesting to know that a small percentage of hydrochloric acid is present in the gastric juice secreted by the glands in the stomach and is necessary in the digestion of our food. Sometimes too much or too little of this acid is secreted, and this causes trouble.

Hydrochloric acid is one of our most useful laboratory reagents. In the industries its largest uses are for cleaning metals which are to be plated or tinned, and in the manufacture of glucose (p. 460) and of glue. Some specially important properties are the following:

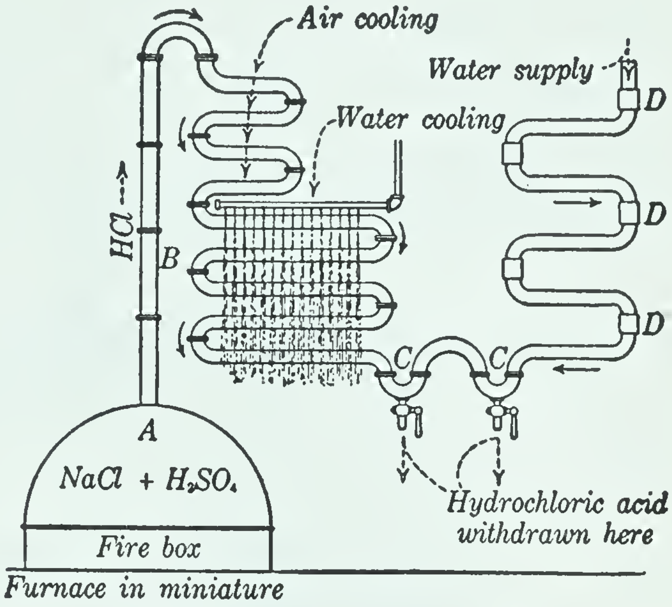


FIG. 161. Commercial preparation of hydrochloric acid

Sodium chloride and sulfuric acid are heated together in the furnace *A*, and the resulting hydrogen chloride escapes through the pipe *B*. It is first air-cooled, then water-cooled, and finally absorbed in water in the traps *C*. Water is renewed from time to time through *D*

1. ***Taste.*** A dilute solution of the acid has a sour taste like that of vinegar.

2. ***Action upon colored compounds.*** It acts upon many colored compounds and changes their color in some way, very often to a red; but it does not bleach them. For example, it changes the blue color of *litmus paper* to red. Litmus is a coloring matter obtained from a plant.

3. ***Action upon metals and their oxides and hydroxides.*** When hydrochloric acid is brought into contact with many of the metals or their hydroxides or oxides, the hydrogen of the acid is replaced (p. 195) by the metal, forming a *chloride*:

$$2\,Na + 2\,HCl \longrightarrow 2\,NaCl + H_2\uparrow$$
$$NaOH + HCl \longrightarrow NaCl + HOH\ (H_2O)$$
$$Zn + 2\,HCl \longrightarrow ZnCl_2 + H_2\uparrow$$
$$ZnO + 2\,HCl \longrightarrow ZnCl_2 + H_2O$$
$$Zn(OH)_2 + 2\,HCl \longrightarrow ZnCl_2 + 2\,H_2O$$

We shall see that all acids have much these same properties.

Test for hydrochloric acid and chlorides. Suppose we wish to know whether a certain liquid is hydrochloric acid or contains some hydrochloric acid along with other substances. The liquid might be water or alcohol, or it might be any number of compounds dissolved in water. What reaction, or *test*, will tell us whether hydrochloric acid is present?

The usual test is the following: We pour some of the liquid into a test tube (Fig. 162), add a few drops of nitric acid, and then two or three drops of a solution of silver nitrate ($AgNO_3$). If hydrochloric acid is present, a white precipitate of silver chloride ($AgCl$) is at once formed in accordance with the following equation:

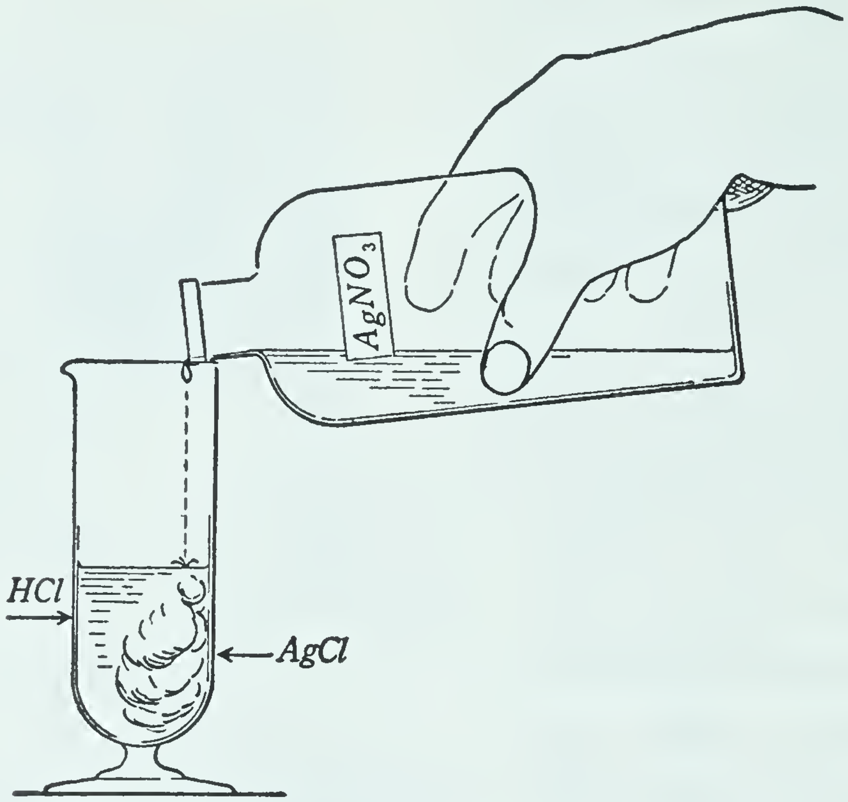


Fig. 162. Testing for hydrochloric acid

A few drops of a silver nitrate solution are added to the solution to be tested

$$AgNO_3 + HCl \longrightarrow AgCl\downarrow + HNO_3$$

The nitric acid added in making the test prevents the silver nitrate from forming a white precipitate with a number of other compounds that might be present. Solutions of chlorides of metals, such as a solution of sodium chloride in water, will also give a precipitate of silver chloride:

$$AgNO_3 + NaCl \longrightarrow AgCl\downarrow + NaNO_3$$

If a white precipitate forms under the conditions just described, it tells us that either hydrochloric acid or a chloride is present. It is a simple matter, however, to distinguish between the two. For example, hydrogen gas is given off when a bit of zinc is added to hydrochloric acid, but not when zinc is added to a solution of a chloride.

Commercial compounds; chemically pure compounds. The product first obtained in the preparation of any compound, especially on a large scale, is certain to contain impurities. It is called a *commercial* product. When these impurities have been removed, the compound is marked *chemically pure*, or simply C. P. For many purposes the commercial product is just as good as the chemically pure, and it is much cheaper.

By-products. In making almost any chemical substance other products are formed as well as the one that is wanted. These are called *by-products*. If a use can be found for them, and the chemist in charge can get them out in usable condition, they add to the profits of the business. If they are of no value, they must be got rid of in some way, and this adds to the cost.

In making chlorine by electrolysis (Fig. 150) both the sodium hydroxide and the hydrogen are by-products and have many commercial uses. So this gives the electrolytic process an advantage over other methods of preparation. In making hydrochloric acid (p. 226) the sodium sulfate left behind is a by-product that has value.

The commercial success of many processes depends very largely on the value of its by-products, and it is an important part of the work of an industrial chemist to hunt up uses for his by-products.

CHAPTER SUMMARY IN QUESTION FORM

1. (*a*) When and by whom was chlorine discovered? (*b*) Why was it named chlorine?

2. What precautions must we take in working with chlorine?

3. Where do we find chlorine (*a*) in the free state? (*b*) in the combined state?

4. (*a*) What is the most abundant compound of chlorine? (*b*) How can we liberate the chlorine from this compound?

5. (*a*) From what compound is chlorine prepared commercially, and by what process? (*b*) What two other substances are prepared at the same time?

6. Compare chlorine and oxygen as to (*a*) weight; (*b*) color; (*c*) odor; (*d*) solubility in water; (*e*) effect when breathed.

7. Is the chlorine that we buy in cylinders in the form of a gas, a liquid, or a solid?

8. What name is given to a compound formed by the union of chlorine with another element?

9. A jet of hydrogen burning in air will continue to burn when the flame is lowered into a jar of chlorine. Name the compound formed when the hydrogen burns (*a*) in air; (*b*) in chlorine.

10. (*a*) Name four elements that combine readily with chlorine. (*b*) Name the compound formed in each case.

11. Name the two important uses of chlorine.

12. How do we explain the fact that chlorine will not bleach most substances unless water is present?

13. (*a*) What name do we give to the state of an element at the instant of its liberation from a compound? (*b*) How do we account for the greater activity of the element in this state?

14. Give the names and formulas of some compounds of chlorine that are used in medicine.

15. (*a*) Name two ways of getting hydrogen chloride. (*b*) Which of these is the cheaper? (*c*) Describe the method used for preparing hydrogen chloride on a commercial scale.

16. How do we distinguish in name between gaseous HCl and its solution in water?

17. Describe hydrochloric acid under the following heads: (*a*) appearance; (*b*) density; (*c*) occurrence in our bodies; (*d*) uses; (*e*) taste; (*f*) action on colored compounds.

18. Describe the action of hydrochloric acid upon metals, their oxides and hydroxides, and give an illustration of each, writing the equations for the reactions.

19. How can you test a solution for the presence (*a*) of hydrochloric acid? (*b*) of a chloride?

20. What is the distinction between (*a*) commercial hydrochloric acid and (*b*) chemically pure hydrochloric acid?

21. (*a*) What is meant by the term *by-product*? (*b*) Give the by-products formed in the commercial preparation of chlorine; (*c*) in the preparation of hydrochloric acid.

THOUGHT QUESTIONS

1. What elements so far studied are found (*a*) free in nature? (*b*) combined? (*c*) both free and combined?

2. Account for the fact that some elements are found free in nature, while others are not.

3. Why do we use one method for the preparation of chlorine in the laboratory, and another for preparing it on a large scale?

4. (*a*) Why do we use one method for collecting oxygen and hydrogen, and another for collecting chlorine and hydrogen chloride? (*b*) Suggest another way of collecting the latter gases.

5. How many electrons are there in the outer (or valence) orbit of the atom of (*a*) chlorine? (*b*) hydrogen? (*c*) oxygen? (*d*) Why should you expect hydrogen to combine with chlorine?

6. What serious trouble would result if you attempted to collect hydrogen chloride over water in the laboratory preparation of this gas?

7. Since you cannot collect hydrogen chloride over water, and since the gas is invisible, how can you tell when the bottle in which you are collecting the gas is filled?

8. The following words apply to hydrochloric acid. Use them in a paragraph of specific statements about this reagent:

solution of
taste
contains the elements
by some metals, for example
litmus

9. (*a*) What is the percentage of chlorine in sodium chloride? (*b*) What weight of sodium chloride would be required in the preparation of 10 tons of chlorine?

10. Suppose you wished to prepare 1 liter of chlorine in order to study its properties. What weight of (*a*) manganese dioxide and of (*b*) hydrogen chloride would be required?

11. (*a*) Write the equation for the reaction that takes place when hydrogen and chlorine combine to form hydrogen chloride. What is the ratio (*b*) between the volumes of hydrogen and chlorine that combine with each other? (*c*) between the volume of either one and that of the hydrogen chloride formed? (Solve (*b*) and (*c*) by Avogadro's law.)

OPTIONAL EXERCISES

1. Design and exhibit to the class a small model showing the principal parts of a Vorce cell for the production of chlorine.

2. Laboratory supply houses sell concentrated hydrochloric acid in bottles containing 2½ liters of the acid. (*a*) Assuming that the acid has a density of 1.19 and contains 38 per cent by weight of hydrogen chloride, calculate the weight of the liquid and the approximate weight of hydrogen chloride in the liquid. (*b*) What weight of sodium chloride would be required in order to prepare this weight of hydrogen chloride?

CHAPTER XX

Sodium and Potassium

[Metals That Are Lighter than Water]

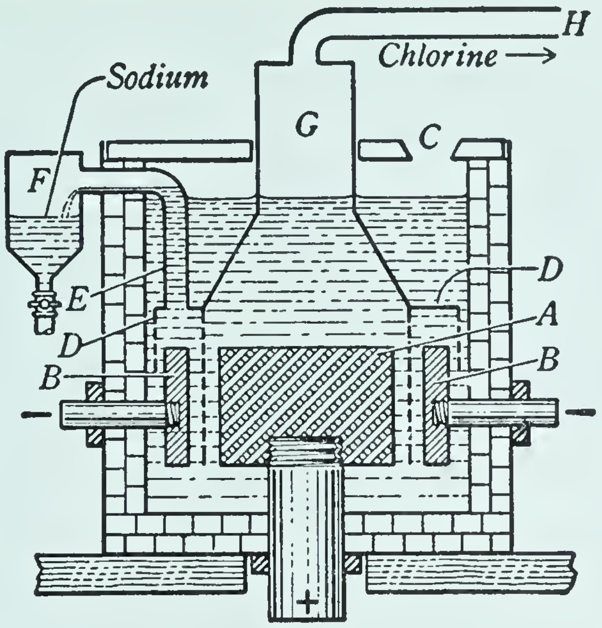
How are elements discovered? There are ninety-two varieties of matter found in nature that all chemists agree are elements. Suppose that you were to find a mineral quite unlike any so far known. Is it a new element? Is it a compound that *contains* a new element? How are you to know? Certainly you cannot decide by the looks of the material. By looking at it no one imagined that the brick-red substance Priestley heated (p. 79) contained the silvery metal mercury and gaseous oxygen.

FIG. 163. Sir Humphry Davy (1778-1829)

A distinguished English scientist who proved that chlorine is an element and who first isolated the elements sodium and potassium

How sodium and potassium were discovered. For a long time chemists had been acquainted with a group of substances that they called *alkalies*, and that they thought were elements. Lavoisier had a theory that made him think all these alkalies were *oxides* of various metals, none of which had ever been obtained. Among these alkalies were *soda* and *potassa*, which we now know contain both oxygen and hydrogen as well as a metal. We call them sodium hydroxide (NaOH) and potassium hydroxide (KOH) respectively.

Now the gifted Sir Humphry Davy (Fig. 163) knew that water, long thought to be an element, had been decomposed by the electric current into oxygen and hydrogen, and he thought it might be possible to decompose the alkalies in this same way. So in 1807 he passed an electric current through melted potassium hydroxide and found "that small globules having a high metallic luster similar in visible char-



The Downs cell (so called from the name of its inventor) is used in the commercial production of sodium from sodium chloride. *A* is the anode (graphite), and *B*, *B*, the annular iron cathode, which is surrounded by the compartment *D*, *D*. The melted sodium chloride is admitted at *C*. When the current is connected, the molten sodium liberated at the cathode *B*, *B*, rises in the compartment *D*, *D*, and flows upward through the tube *E* and over into the compartment *F*, from which it is withdrawn from time to time. The chlorine escaping from the anode *A* rises in the dome *G* and escapes through the pipe *H*

Fig. 164. A Downs cell for the electrolytic production of metallic sodium

acter to quicksilver appeared." This was the metal we now call potassium, and it was the first metal to be made by electrolysis. A few days later Davy prepared the metal sodium from sodium hydroxide in the same way.

Where sodium and potassium are found. These two elements are far too active to be found in the free state in nature, but their compounds are abundant and of many kinds. Of these sodium chloride (NaCl) is the most plentiful and the easiest to get. Not only is it the chief salt in sea water but it is found in immense solid deposits in many places in the world and is often mined, much as coal is mined.

While potassium compounds are less abundant than those of sodium, yet large deposits occur in Germany and France, as well as in New Mexico, Texas, and California. These deposits are of great value, because potassium compounds are essential constituents of fertilizers.

How we get sodium and potassium. Davy got sodium over a hundred years ago by the electrolysis of sodium hydroxide. We get it today in the same general way; only we use sodium chloride instead of the hydroxide, and we use apparatus suited to large-scale production. The method is described in connection with the Downs cell (Fig. 164). It will be seen that chlorine is a by-product in this method.

Potassium can be made by electrolysis in this same general way; but its preparation is more difficult, it costs more, and sodium is just as good for most purposes.

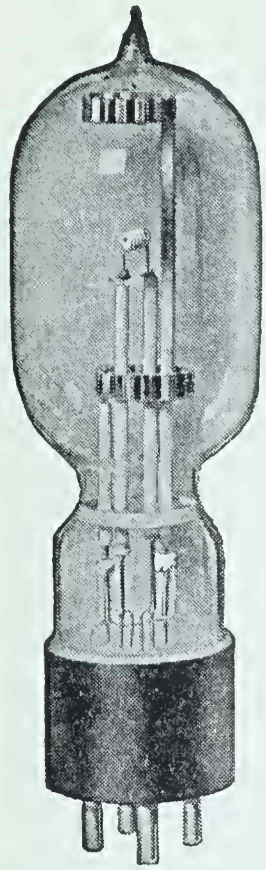


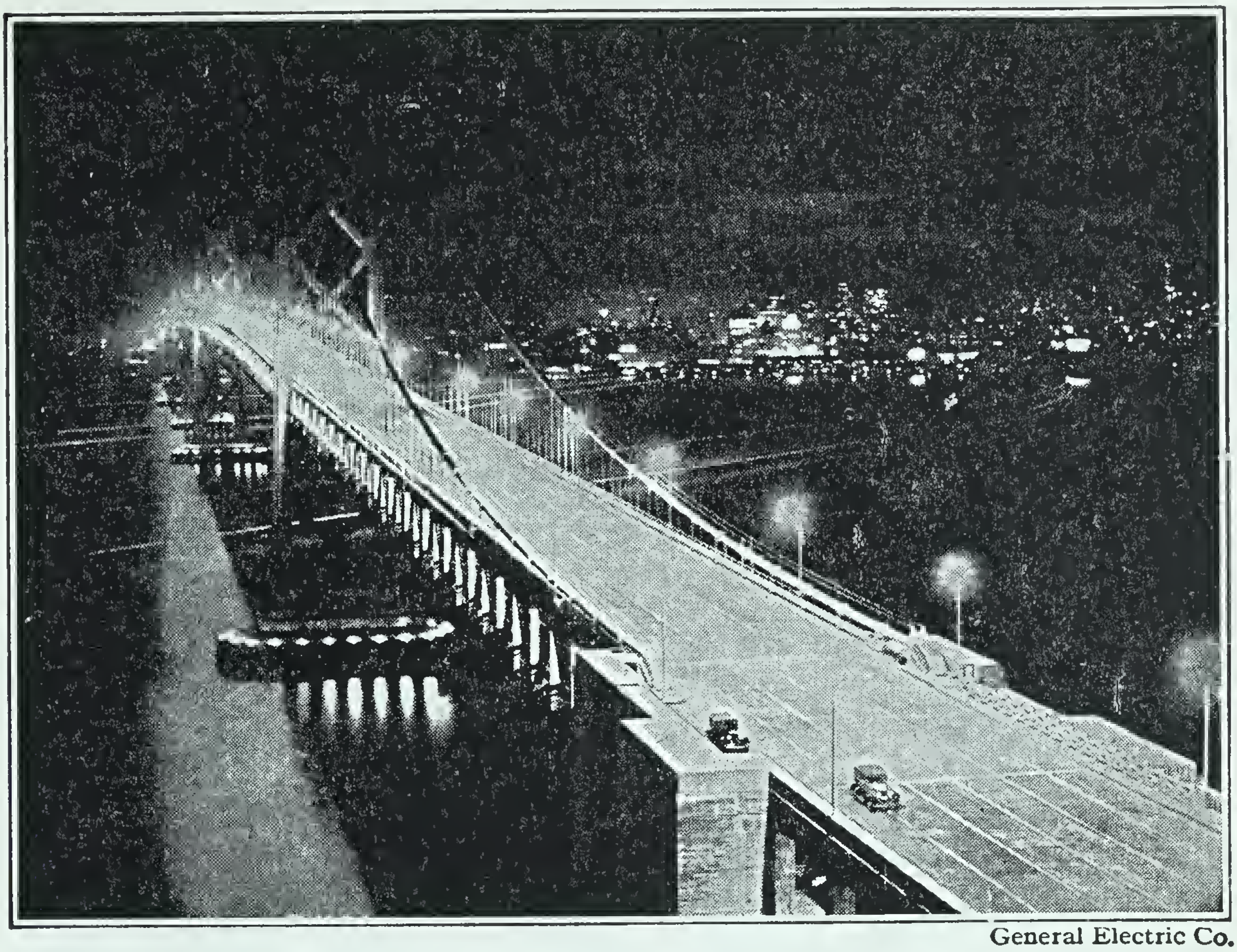
Fig. 165. A sodium-vapor lamp

The sodium-vapor lamp. Sodium has many uses in the making of a variety of chemical compounds. It is finding a most interesting use in one of the newest kinds of electric-light bulbs. Everyone is familiar with the red and blue and green electric advertising signs that make our business streets look so colorful. These signs are made of glass tubes that have nothing in them but a very small quantity of some gas (chiefly neon) or vapor that gives the color.

In each case the colored light is caused by electrons jumping off the atoms of the gas and coming back to their places again, much like bees in a busy hive. The electrical current gives the electrons enough energy to let them break away from the atom, and as they come back they give off this energy in part as colored light, the color depending on the structure of the atom. So by the use of different gaseous elements different colors are obtained.

Now sodium vapor (supplied by a little metallic sodium in the lamp) gives a pure yellow light, and the human eye is more sensitive to this color than to any other. So the sodium lamp (Fig. 165) makes things look more distinct than any other lamp, and it is especially well suited to highway lighting (Fig. 166). It uses much less current (is much more efficient) than the best wire-filament lamps. The sodium in the lamp vaporizes when the lamp becomes warm; a little neon is also put into the bulb with the sodium, to carry the current till the lamp is warmed up.

What sodium and potassium are like. When Davy first prepared sodium and potassium, he was struck by two things: they both have the silvery appearance of a metal, and yet they are very light and low-melting. They are slightly lighter than water and melt below water's boiling point.



General Electric Co.

FIG. 166. A night view of the Oakland-San Francisco Bridge. It is eight and a half miles in length and is lighted by sodium-vapor lamps

But we shall find that it is neither the density nor the melting point but its chemical conduct that determines whether an element is a metal; and by this standard both sodium and potassium are typical metals. They oxidize very rapidly in the air, and are kept under kerosene (Fig. 167), since they are heavier than kerosene and do not act upon it. They displace hydrogen from water (p. 103) and, like zinc, from certain acids (p. 104).

Valence of sodium and of potassium. Like hydrogen, both sodium and potassium have but one valence electron (Fig. 168) and are therefore positive univalent elements. They give up their valence electrons even more readily than does hydrogen, and it is for this reason that they displace hydrogen from water and acids.

Sodium hydroxide (or caustic soda) (NaOH). Someone has said that the state of civilization of a nation can be told from the amount of soap it uses. He might just as truly have said, from the amount of sodium hydroxide it uses; for this is used in the manufacture of nearly all our soaps. Measured on such a scale the United States ranks high; for each year it uses more than a million and a half tons of soap. In addition we use sodium hydroxide in making paper, rayon, and cellophane, in refining petroleum, and for many other purposes (Fig. 169). In the laboratory it is one of our most used reagents. Evidently this compound is of very great importance.

SODIUM
IN
KEROSENE

FIG. 167. Sodium

In our laboratories it is kept in kerosene

Sodium hydroxide is a very active compound. It is a white solid (Fig. 170), and when exposed to the air it rapidly absorbs moisture and carbon dioxide from the air. It is very soluble in water, and it is this solution that is commonly used. When brought into contact with the skin, it acts as a caustic; that is, it burns or shrivels the skin. This is why it is called *caustic* soda. As an article of household use it is called *lye*, a name shared by potassium hydroxide, KOH.

These compounds are often used to open the drains of kitchen sinks stopped up with grease. Potassium hydroxide should be used for this purpose; for it changes the grease into a soft soap, easily washed away. Sodium hydroxide makes a hard soap likely to stay in the pipe.

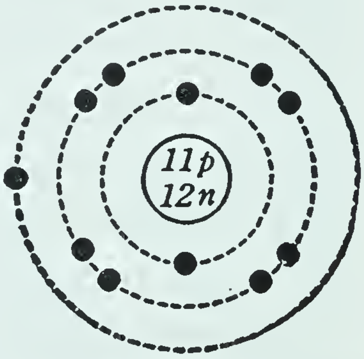


FIG. 168. The structure of the sodium atom

How sodium hydroxide and potassium hydroxide are made. Sodium hydroxide is made commercially by two different processes, as follows:

1. In the older process sodium carbonate is treated in solution with calcium hydroxide (slaked lime, $Ca(OH)_2$). Calcium carbonate is precipitated as an insoluble solid, according to the equation

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + 2\ NaOH$$

The dilute solution of sodium hydroxide, filtered from the insoluble calcium carbonate, is evaporated to dryness, and the solid is then melted and poured into molds to solidify.

2. The newer method is by the electrolysis of a solution of sodium chloride as explained under "Chlorine" (p. 220); so every chlorine plant is also a plant for producing sodium hydroxide, as is shown in Fig. 150.

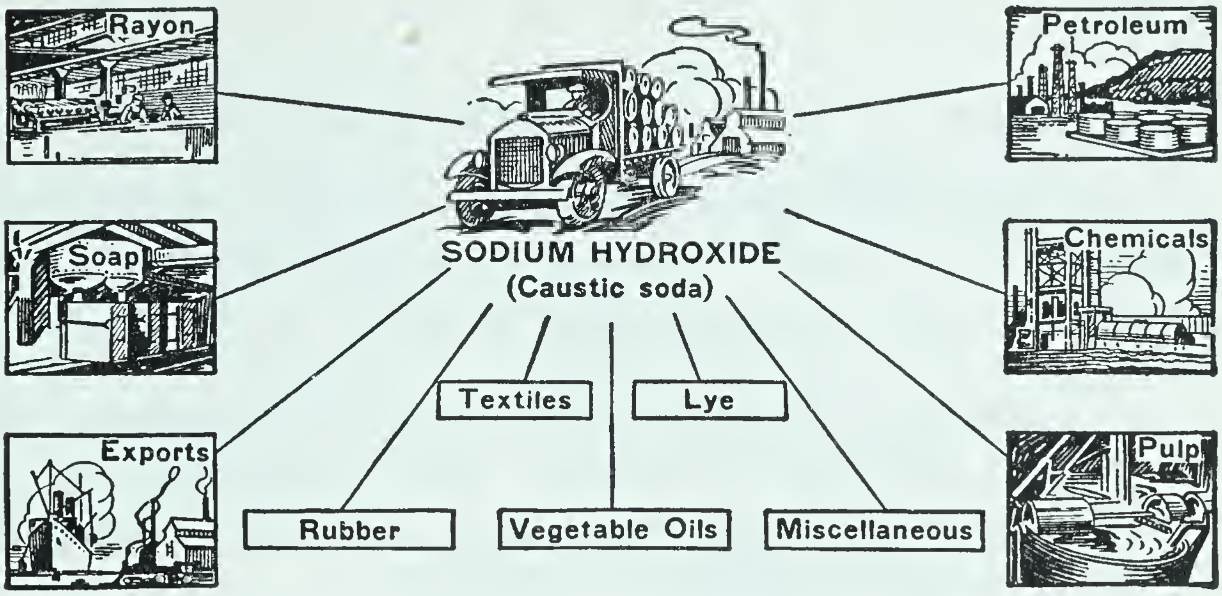

Rayon
Petroleum
Soap
SODIUM HYDROXIDE
(Caustic soda)
Chemicals
Textiles
Lye
Exports
Pulp
Rubber
Vegetable Oils
Miscellaneous

Fig. 169. The more important uses of sodium hydroxide

Potassium hydroxide (caustic potash) (KOH). Potassium hydroxide is prepared in the same way as sodium hydroxide, and resembles it closely in nearly all properties. Since the sodium hydroxide is cheaper, it is more widely used.

Chemical conduct. Both sodium hydroxide and potassium hydroxide have certain properties in common with the hydroxides of many of the other metals. These are as follows:

1. *Action on litmus.* Solutions of them act on litmus (as well as on certain other colored substances) in just the opposite way from the acids (p. 227); in other words, they turn red litmus blue.

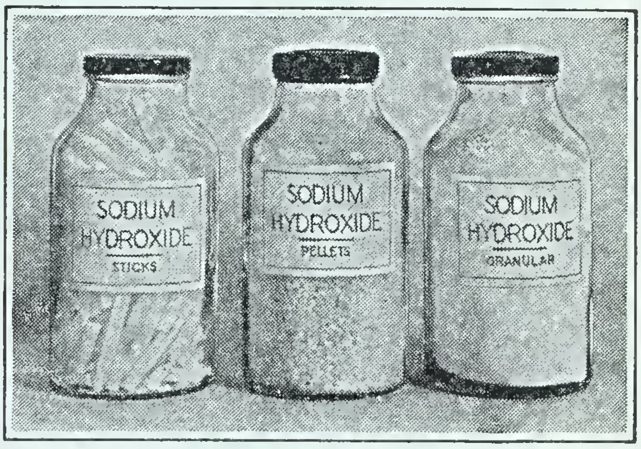

SODIUM
HYDROXIDE
STICKS
SODIUM
HYDROXIDE
PELLETS
SODIUM
HYDROXIDE
GRANULAR

Fig. 170. You can buy sodium hydroxide in sticks, small pieces, a powder, or a solid chunk

2. *Action on acids.* When brought into contact with acids the metal of the hydroxide changes places with the hydrogen of the acids:

$$NaOH + HCl \longrightarrow NaCl + HOH\ (H_2O)$$
$$KOH + HCl \longrightarrow KCl + HOH\ (H_2O)$$

In the following chapter we shall find that these hydroxides belong to a very important class of compounds called *bases.*

CHAPTER SUMMARY IN QUESTION FORM

1. (*a*) Who discovered sodium and potassium? (*b*) What fact suggested the experiment which led to their discovery?

2. Name the most important compound of sodium found in nature.

3. (*a*) Where do we find large deposits of potassium compounds? (*b*) What is the chief use of these compounds?

4. (*a*) Give the method for preparing sodium and potassium. (*b*) Which is the more difficult to prepare?

5. (*a*) In what respects does sodium resemble silver in physical properties? (*b*) In what respects does it differ?

6. How can sodium hydroxide be prepared (*a*) from sodium carbonate? (*b*) from sodium chloride?

7. By what other name is sodium hydroxide known (*a*) in the chemical laboratory? (*b*) in our homes?

8. What are the chief uses of sodium hydroxide?

9. Give the action of sodium hydroxide and of potassium hydroxide on (*a*) litmus; (*b*) acids. (*c*) Illustrate their reaction on acids by equations.

10. The following words apply to sodium hydroxide and potassium hydroxide. Put them in a paragraph of specific statements about these two compounds:

very soluble in
litmus
when brought in contact with acids
exchange

THOUGHT QUESTIONS

1. Write the equations for the reaction of sodium on each of the following: (*a*) water; (*b*) sulfuric acid; (*c*) hydrochloric acid; (*d*) oxygen (formula for oxide formed, Na_2O_2).

2. (*a*) Explain why water must not be present in the preparation of sodium. (*b*) Name two substances that would be formed in case water were present.

3. (*a*) Which are the more important commercially, sodium and potassium or their compounds? (*b*) Give the reason for your answer.

4. An industrial plant that prepares sodium carbonate is very likely to prepare sodium hydroxide also. Explain.

5. What two properties has kerosene that make it suitable for preserving sodium?

6. 100 ml of a molar solution of sodium hydroxide was added to 100 ml of a molar solution of hydrogen chloride, and the resulting liquid evaporated to dryness. (*a*) What compound remained? (*b*) Calculate its weight.

7. Suppose you wished to prepare 100 lb of sodium hydroxide by the older process. (*a*) What compounds should you need? (*b*) Calculate the weight of each that would be required.

OPTIONAL EXERCISES

1. About 600 tons of chlorine are prepared daily in the United States by the electrolysis of sodium chloride. (*a*) What weight of sodium chloride is required? (*b*) What weight of sodium hydroxide is formed in the process? (*c*) What weight of hydrogen?

2. 100 ml of a molar solution of sodium hydroxide was added to 50 ml of a molar solution of hydrogen chloride, and the resulting liquid was evaporated to dryness. (*a*) What compounds remained? (*b*) Calculate the weight of each.

3. Plan and construct a small model showing the principal parts of a Downs cell for the production of sodium.

CHAPTER XXI

Acids, Bases, and Salts

[The Three Most Important Groups of Compounds]

We must get the compounds into classes. We have seen (p. 26) that chemists have found and described such a vast number of compounds that it is hopeless to study them all one by one. We must arrange them in groups, or classes, and learn the general character of each class. Then we can study more carefully a few compounds in each class.

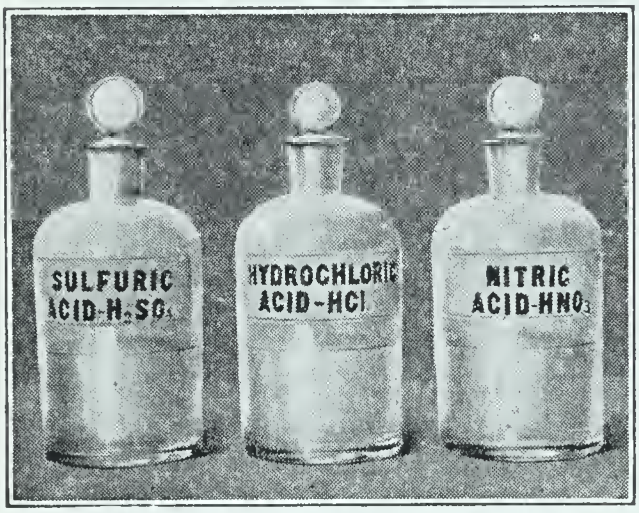
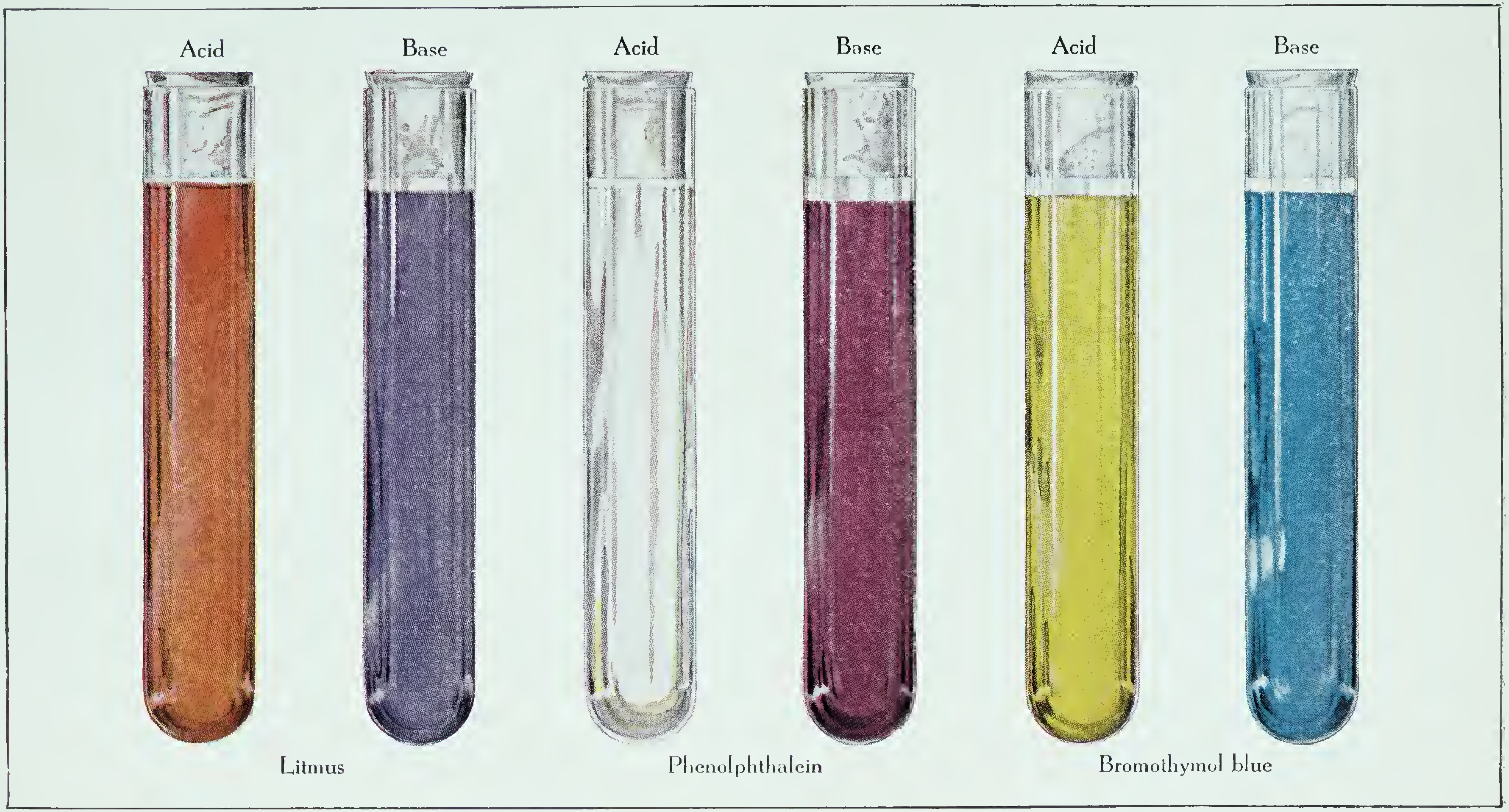


FIG. 171. The three common acids

We have already broadly classified all matter into elements, compounds, and mixtures. We can subdivide compounds in many different ways, but most of those that we shall study belong to one or another of the three groups *acids*, *bases*, and *salts*. We have studied one *acid* (hydrochloric acid) and one *base* (sodium hydroxide). To these we must add the third group, called *salts*.

Acids. In addition to hydrochloric acid two other acids, sulfuric and nitric acid (Fig. 171), are in constant use in every laboratory and in many industries. Sulfuric acid is a solution, in water, of an oily, colorless liquid called *hydrogen sulfate* (H_2SO_4); nitric acid is a similar solution of a colorless liquid called *hydrogen nitrate* (HNO_3). Two other acids, phosphoric acid (H_3PO_4) and carbonic acid (H_2CO_3), will be mentioned many times later on. We rarely need to distinguish between these pure compounds and their solutions in water. Both are called acids for convenience, but it is only their solutions in water (or in a few other liquids) that have the properties all acids have in common.

Properties common to all acids. The properties common to all acids are in the main those given for hydrochloric acid (p. 227). In a general way we may describe them as follows.


Acid
Base
Acid
Base
Acid
Base
Litmus
Phenolphthalein
Bromothymol blue

THE ACTION OF ACIDS AND BASES ON THREE TYPICAL INDICATORS

An acid is a compound of hydrogen whose solution in water (1) has a sour taste, (2) changes blue litmus to red, and (3) acts on many metals and their hydroxides, forming compounds in which the hydrogen atoms of the acids are replaced by atoms of the metal.

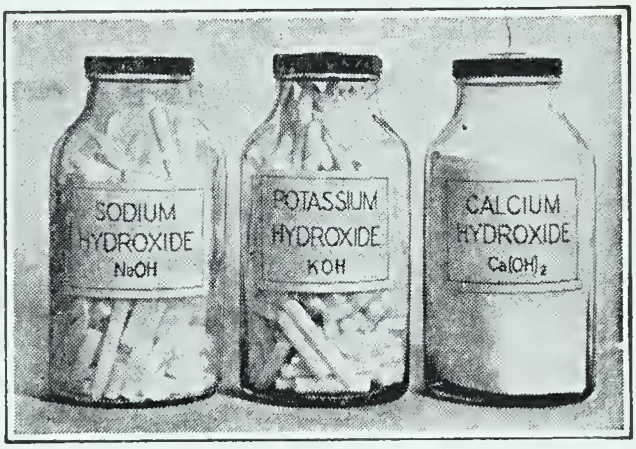


Fig. 172. The three common bases

Acids differ greatly from one another. All the students in a class resemble each other in a few ways, but in all other respects each one has his own personal traits. Similarly the acids, alike in a few ways, have each their own special sets of properties. Some acids are very stable, others are easily decomposed; some have color, others are colorless; some are very poisonous, others are harmless and may even be useful as food. Some are not even sour to the taste. Apples and pears contain malic acid, and oranges, lemons, and grapefruit contain citric acid. All soluble acids are electrolytes.

Bases: the opposite of acids. The hydroxides of the metals are called *bases.* Some of these are very soluble in water, a fact which is true of sodium hydroxide and potassium hydroxide. Others, like calcium hydroxide ($Ca(OH)_2$), are only slightly soluble, while still others, like aluminum hydroxide ($Al(OH)_3$), are insoluble (Fig. 172). Those that are soluble act on litmus (and certain other colored substances) in just the opposite way from acids; that is, their solution turns red litmus blue. All soluble bases are electrolytes.

The most important thing about bases is their action on acids. When a base and an acid are brought together, the hydrogen atoms of the acid are replaced by the metal atoms of the base:

$$HCl + NaOH \longrightarrow NaCl + HOH\ (H_2O)$$

We may now describe a base as follows.

A base is a compound of a metal and one or more OH groups, the number depending on the valence of the metal. It reacts with an acid, forming a compound in which the hydrogen *atoms of the acid are replaced by the metal atoms of the base. If it is soluble in water, the solution turns red litmus blue.*

Alkalies. *Alkali* is an old Arabian name for sodium hydroxide and potassium hydroxide, which were long thought to be the same thing. The name is now used to include sodium hydroxide, potassium hydroxide, and other very soluble and strong bases as well.

Salts; neutralization. We have seen that when an acid and a base are brought together, a reaction of double replacement (p. 195) takes place in which the hydrogen atoms of the acid and the atoms of the metal of the base change places. The following are examples:

$$\begin{aligned} HCl + NaOH &\longrightarrow NaCl + HOH\ (H_2O) \\ 2\ HCl + Ca(OH)_2 &\longrightarrow CaCl_2 + 2\ HOH \\ H_2SO_4 + 2\ NaOH &\longrightarrow Na_2SO_4 + 2\ HOH \end{aligned}$$

In all such reactions as these the acid and the base are said to *neutralize* each other, because each loses its characteristic properties. The compound formed, other than water, is called a *salt.* An examination of the formulas of the salts will show that in composition they differ from the acids in that the molecules of the salt contain a metal atom in place of one or more hydrogen atoms. All soluble salts are electrolytes. We may describe a salt as follows.

A salt is a compound derived from an acid by replacing the hydrogen atoms of the acid by atoms of a metal.

Number of salts. From what has been said, we should expect each acid to form as many salts as there are metals; and in general this is true. In a few cases the expected salts are unstable and cannot be made, but the number of salts that can be derived from most acids is large. The following equations show the formation of some typical salts made by neutralizing sulfuric acid:

$$\begin{aligned} H_2SO_4 + 2\ NaOH &\longrightarrow Na_2SO_4 + 2\ H_2O \\ H_2SO_4 + Ca(OH)_2 &\longrightarrow CaSO_4 + 2\ H_2O \\ H_2SO_4 + Fe(OH)_2 &\longrightarrow FeSO_4 + 2\ H_2O \\ 3\ H_2SO_4 + 2\ Al(OH)_3 &\longrightarrow Al_2(SO_4)_3 + 6\ H_2O \end{aligned}$$

Monobasic and dibasic acids. Acids, like hydrochloric and nitric acids, that have only one replaceable hydrogen atom in the molecule are called *monobasic acids*. Acids, like sulfuric acid, that have two replaceable hydrogen atoms in each molecule are called *dibasic acids*. Similarly we may have *tribasic* and *tetrabasic acids*.

Normal and acid salts. From acids that contain two or more replaceable hydrogen atoms, two different classes of salts may be derived: one class in which *all* the hydrogen of the acid has been replaced by a metal, and one in which only a *part* of the hydrogen has been replaced. Thus, from sulfuric acid we may obtain the two sodium salts, Na_2SO_4 and $NaHSO_4$, as shown in the following equations:

$$H_2SO_4 + 2\ NaOH \longrightarrow Na_2SO_4 + 2\ H_2O$$
$$H_2SO_4 + NaOH \longrightarrow NaHSO_4 + H_2O$$

Those salts that are derived from an acid by displacing *all* the hydrogen present, such as Na_2SO_4, are called *normal salts*, while those derived from an acid by displacing only a part of the hydrogen, like $NaHSO_4$, are called *acid salts*. Acid salts are so called because in solution they act both like a salt and like an acid. A metal has replaced hydrogen of an acid, and to this extent the resulting compound is a salt. But the compound still contains replaceable hydrogen and so is an acid.

Basic salts. If a molecule of a base has two or more hydroxyl groups, one may be replaced by an acid group, while the others are not. This will give us a *basic salt*. For example, we have basic lead nitrate:

$$Pb(OH)_2 + HNO_3 \longrightarrow Pb(OH)(NO_3) + H_2O$$

Indicators. We have seen that acids turn blue litmus to a red color, while bases turn the red back to blue. So we may employ litmus to find out whether a given solution is acid or basic. It may also be used to test whether or not a solution is neutral (that is, neither acid nor basic); for such solutions will have no effect on either blue or red litmus. A color material that changes color in this way is called an *indicator* (see illustration facing page 240). Some blue flowers, red fruit juices, or even red cabbage leaves may be used as *indicators.* Red spots on blue clothes in the laboratory are convincing though unpleasant proofs of the way indicators act. Such spots, if produced by acids, should be turned blue again with a weak base (ammonia water).

Radicals. When we study the formulas of various molecules, we sometimes notice a group of two or more atoms that seem to fit together and form a natural unit.

For example, if we compare the formulas H_2SO_4, Na_2SO_4, $Al_2(SO_4)_3$, it will be seen that they all have the group of atoms SO_4. All the bases, illustrated by the formulas NaOH, KOH, $Ca(OH)_2$, $Al(OH)_3$, have the group of atoms OH.

A group of atoms which act together as a unit in chemical reactions is called a radical.

The group SO_4 is called the *sulfate radical*; the group OH is called the *hydroxyl radical.*

Valence of radicals. Radicals, like atoms, have valence; that is, they tend to gain or lose electrons. We can tell the valence of a radical from the formulas of the compounds in which it is present, just as we can tell the valence of an atom. The hydroxyl radical is univalent, as is shown by the formulas NaOH, KOH, HOH, the atoms Na, K, and H being univalent. The sulfate radical (SO_4) is bivalent, as is shown by the formulas H_2SO_4, Na_2SO_4, $CuSO_4$; for it combines with two univalent atoms (H or Na) or with one bivalent atom (Cu).

The arrangement of electrons in a radical. The student will be wondering how the electrons are arranged in a radical such as univalent hydroxyl, OH. Fig. 173 is a diagram of the hydrogen atom; Fig. 174, of the oxygen atom; and Fig. 175, of the hydroxyl radical. For convenience we may represent the hydrogen and oxygen atoms as $H\cdot$ and $\cdot\overset{..}{\underset{..}{O}}\cdot$, *in which the dots represent the valence electrons only.*

In the univalent hydroxyl radical the atoms and their valence electrons are arranged as indicated by the symbol $\cdot\overset{..}{\underset{..}{O}}:H$. You will see that by sharing a pair of electrons hydrogen has its orbit of two full, while the oxygen atom needs only to get one more electron (by capture or by sharing) to complete its valence orbit of 8. So the hydroxyl radical is univalent.

In the water molecule, $\mathrm{H}:\overset{..}{\underset{..}{\mathrm{O}}}:\mathrm{H}$, the extra electron was captured from a second hydrogen atom. In sodium hydroxide, $\mathrm{Na}:\overset{..}{\underset{..}{\mathrm{O}}}:\mathrm{H}$, the electron was captured from a sodium atom. Compounds with radicals of this kind are electrovalent (polar) compounds (p. 204).

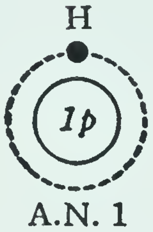


Fig. 173. The hydrogen atom

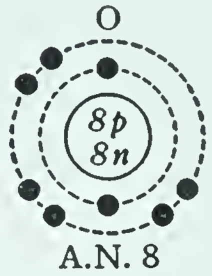


Fig. 174. The oxygen atom

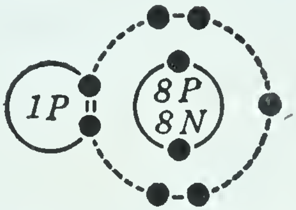


Fig. 175. The hydroxyl radical

Common Radicals with Their Valences

Name	Formula	Valence
Ammonium radical	NH_4	+ 1
Nitrate radical	NO_3	− 1
Hydroxyl radical	OH	− 1
Carbonate radical	CO_3	− 2
Sulfate radical	SO_4	− 2
Phosphate radical	PO_4	− 3

Formulas of molecules containing radicals. In the formula of a compound we want to show the *radical* as a part of the compound just as we do the various *atoms*. Calcium is a bivalent element; so we write the formula of its hydroxide $Ca(OH)_2$ (corresponding to its chloride, $CaCl_2$) rather than CaO_2H_2, which does not show the radical OH. Aluminum is a trivalent element, and we write the formula of its hydroxide $Al(OH)_3$. The formula of its sulfate is written $Al_2(SO_4)_3$, not $Al_2S_3O_{12}$.

Formulas of salts. When we know the valence of a metal and the formula of any acid or its radical, it is easy to write the formula of the salt which the metal may be expected to form with the acid. For example, suppose we wish to write the formulas of the salts which the bivalent metal calcium forms with the three acids HCl, H_2SO_4, and H_3PO_4. First write the symbol of the element in place of the hydrogen of the acid:

$$CaCl \qquad\qquad CaSO_4 \qquad\qquad CaPO_4$$

Now write over the symbols of calcium, chlorine, and each of the radicals SO_4 and PO_4 the valence of each element or radical:

$$\overset{2}{Ca}\overset{1}{Cl} \qquad\qquad \overset{2}{Ca}\overset{2}{SO_4} \qquad\qquad \overset{2}{Ca}\overset{3}{PO_4}$$

Finally take such numbers of the two parts of each salt as will add up an equal number of valences. This gives the following as the correct formulas:

$$\overset{2}{Ca}\overset{2}{Cl_2} \qquad\qquad \overset{2}{Ca}\overset{2}{SO_4} \qquad\qquad \overset{6}{Ca_3}\overset{6}{(PO_4)_2}$$

After a little practice anyone can derive these formulas without writing down the different steps.

How acids, bases, and salts are named. It would often be very convenient for us if we had some way of knowing a person's name, even though we may never have met him before. Chemists are able to do this very thing with their compounds. They have made rules for naming them, including the acids, bases, and salts, so that if we are given the formula of a compound we can nearly always tell whether it belongs to any one of these three groups and what its name should be. The rules for naming acids, bases, and salts are as follows:

The names of acids. All the common acids contain either two elements or three elements. Those that contain but two elements are called *binary acids* and are given names made up of the prefix *hydro-* (short for "hydrogen"), the name of the second element present (shortened if necessary), and the ending *-ic*. Examples: HCl, hydrochloric acid; H_2S, *hydrosulfuric* acid.

Acids that contain three elements are called *ternary acids*. Most of these contain oxygen in addition to hydrogen, and it is the third element that gives its name to the acid. It is the chlorine in $HClO_3$ that gives its name to the acid, and the sulfur in H_2SO_4. It usually happens that the same three elements can unite in different proportions to form two or more acids. The most familiar one of these is given a name ending in *-ic*. For example, $HClO_3$ is called *chloric* acid, and H_2SO_4 *sulfuric* acid. The name of the acid containing one less atom of oxygen than the *-ic* acid is given the ending *-ous*. If more than two acids are known, use is made of the prefixes *per-*, meaning "more," and *hypo-*, meaning "less." Examples:

ACID	FORMULA	ACID	FORMULA
Hypochlorous	$HClO$	Hyposulfurous	H_2SO_2
Chlorous	$HClO_2$	Sulfurous	H_2SO_3
Chloric	$HClO_3$	Sulfuric	H_2SO_4
Perchloric	$HClO_4$	Persulfuric	H_2SO_5

The names of bases. All bases have the common name *hydroxide*. They are distinguished from each other by the name of the metal present. Example: NaOH, *sodium hydroxide*; $Ca(OH)_2$, *calcium hydroxide*.

The names of salts. A salt of a binary acid is given a name made up of the names of the two elements in it, with the ending *-ide*. Example, NaCl, *sodium chloride*.

A salt of a ternary acid is named from the acid of which it is a salt. An acid name ending in *-ic* gives a salt name ending in *-ate*; an acid name ending in *-ous* gives a salt name ending in *-ite*. The following table, giving a number of examples, will make the application of these principles clear:

ACID	FORMULA	SODIUM SALT	FORMULA
Hydrochloric	HCl	Sodium chloride	$NaCl$
Hypochlorous	$HClO$	Sodium hypochlorite	$NaClO$
Chlorous	$HClO_2$	Sodium chlorite	$NaClO_2$
Chloric	$HClO_3$	Sodium chlorate	$NaClO_3$
Perchloric	$HClO_4$	Sodium perchlorate	$NaClO_4$

Acid salts are often designated by the prefix *bi-*; for example, $NaHSO_4$ is called sodium *bisulfate*. It is also called sodium acid sulfate, and sometimes sodium hydrogen sulfate.

Carbonic acid (H_2CO_3). In our study of carbon dioxide we learned that when this gas is passed into water, a little of it combines with the water to form the compound H_2CO_3, called *carbonic acid* (p. 153). We will note its properties.

Carbonic acid is a very weak acid; for it has no sour taste, and it barely changes the color of blue litmus. It is a very *unstable* acid. It exists only in water solution, and even then it nearly all breaks up into carbon dioxide and water:

$$H_2CO_3 \longrightarrow H_2O + CO_2\uparrow$$

However, it acts on bases, and gives salts called *carbonates.*

The carbonates. The carbonates are stable solids, for the most part insoluble in water. Many of them are found in nature as rock formations; and these are of great value, as we shall find later on. Limestone is mainly calcium carbonate ($CaCO_3$), while white marble is the nearly pure crystalline salt. Ordinary baking soda and washing soda are soluble sodium carbonates.

When a carbonate is treated with almost any acid, carbon dioxide is given off as a gas (p. 149). For example, when calcium carbonate is treated with hydrochloric acid, carbon dioxide is evolved in accordance with the following equation:

$$CaCO_3 + 2\,HCl \longrightarrow CaCl_2 + H_2O + CO_2\uparrow$$

Since there is an easy test for carbon dioxide (p. 153), we can always tell in this way whether a given material is a carbonate or has a carbonate mixed with it.

CHAPTER SUMMARY IN QUESTION FORM

1. Most of the compounds we shall study belong to one of three groups. Name these groups.

2. (*a*) Name three common acids and (*b*) give their formulas.

3. Name the element common to all acids.

4. State three properties common to acids.

5. Name three ways in which acids may differ from each other.

6. What name do we give to the hydroxide of a metal?

7. Name three properties common to soluble bases.

8. By what other name are the more soluble bases known?

9. Write the formula for (*a*) an important acid; (*b*) an important base. (*c*) Now write the equation for the reaction that will take place when these two compounds are brought together.

10. Write a sentence that tells in general terms what takes place when an acid and a base react together.

11. The hydrogen of an acid is replaced by a metal. To what group does the resulting compound belong?

12. In general, how many salts can be derived from any one acid?

13. How can we tell whether a given liquid is (*a*) acid, (*b*) basic, or (*c*) neutral?

14. (*a*) Distinguish between monobasic, dibasic, and tribasic acids. (*b*) Give an example of each.

15. (*a*) Distinguish between normal salts and acid salts, and (*b*) give an example of each.

16. (*a*) What does the chemist mean by an *indicator*? (*b*) Of what use is it? (*c*) Name a very common one.

17. (*a*) What name do we give to a group of atoms that act together as a unit in a chemical reaction? (*b*) Give an example to illustrate.

18. (*a*) Name each of the following groups of atoms: OH; SO_4. (*b*) How can you determine the valence of each of these groups?

19. Calcium is bivalent. Illustrate how we may find the formulas of the salts that we should expect calcium to form with each of the following acids: HCl; H_2SO_4; H_3PO_4.

20. What name do we give to the action of an acid on a base or vice versa?

21. The following words apply to the reaction between acids and bases. Include them in a paragraph about acids and bases:

neutralize indicator salt and water

22. How many elements are present in (*a*) a binary acid? (*b*) a ternary acid?

23. Illustrate the method of naming binary acids by giving the names of the following: (*a*) HCl; (*b*) H_2S; (*c*) HBr.

24. (*a*) Name the two elements that are present in most ternary acids. (*b*) Which one of the elements present in a ternary acid gives its name to the acid?

25. State what element gives its name to each of the following acids: (*a*) H_2SO_4; (*b*) H_3PO_4; (*c*) H_2CO_3.

26. Distinguish by name between the following acids: H_2SO_4 and H_2SO_3; $HClO_3$ and $HClO_4$; H_3PO_4 and H_3PO_3.

27. What word is common to the names of all bases?

28. Name the following salts and tell how each name is derived: $NaCl$, KCl, $CaSO_3$, Na_2SO_4, $NaHSO_4$, $ZnSO_4$, Na_2CO_3, $NaHCO_3$.

THOUGHT QUESTIONS

1. Classify the compounds represented by the following formulas as acid (monobasic, dibasic, or tribasic), base, or salt (acid or normal): KNO_3, H_2SO_4, $NaHSO_4$, $Al(OH)_3$, HNO_3, KOH, H_2CO_3, H_3PO_4, $NaHCO_3$, $CaSO_4$.

2. Select two acids and five metals, and predict the number of salts that the metals might be expected to form with the acids.

3. State the effect of the following on both colors of litmus paper: (*a*) hydrochloric acid; (*b*) a solution of sodium hydroxide; (*c*) a solution made by adding a gram-molecular weight of hydrochloric acid to a gram-molecular weight of sodium hydroxide.

4. Prepare a table of four columns. At the top of the first column write the word *acid*; and at the top of columns two, three, and four write, respectively, the formulas of sodium hydroxide, calcium hydroxide, and aluminum hydroxide. Now write the formulas of three well-known acids in the first column, and opposite the formula of each acid the formula of the salt that would be formed by the action of the acid on the base.

5. (*a*) Suppose that you had a solution containing a gram-molecular weight of sodium hydroxide. What weight of hydrogen chloride would be required to neutralize it? (*b*) Suppose that after adding the necessary hydrogen chloride you evaporated the solution to dryness. What compound would be left? Calculate its weight.

6. (*a*) Suppose you were to discover four acids having the following formulas: $HBrO$; $HBrO_2$, $HBrO_3$, $HBrO_4$. In accord with the regular rules, what would you name each? (*b*) Name the sodium salts of each.

OPTIONAL EXERCISES

1. Complete and balance the following equations:

$HNO_3 + KOH \longrightarrow$ $\qquad$ $H_3PO_4 + Al(OH)_3 \longrightarrow$

$H_2SO_4 + Ca(OH)_2 \longrightarrow$ $\qquad$ $HCl + Mg(OH)_2 \longrightarrow$

$HNO_3 + Ba(OH)_2 \longrightarrow$ $\qquad$ $H_2SO_4 + Fe(OH)_3 \longrightarrow$

2. Test samples of common substances, such as the following, to see whether their solutions are acid, basic, or neutral in reaction: vinegar; washing soda; borax; sugar; tooth paste; saliva; baking soda; cream of tartar; lemon juice; soil from low, wet, shady places; soil from a well-cultivated, sunny field or garden.

CHAPTER XXII

Ionization

[Why Solutions Conduct the Electrical Current]

Putting things together. Some people like to gather many *facts* so that they can answer questions as a dictionary does: hydrogen burns; acids taste sour; copper is a good conductor of electricity, sulfur is not; a metal handle on a coffeepot gets hot, a wooden one does not. Other people are more like a detective at his work. He too gets all the facts he can, but they all have to do with one thing — his case. Then he makes his guess as to who the guilty one is, and he hunts further for other facts to prove whether his guess is right. The facts are all important; the story he makes from them solves the mystery.

In every science we work like the detective, and in this chapter we shall be putting a number of facts together to solve some chemical mysteries.

Some facts left unexplained. In earlier pages we have left a good many facts without any explanation of them. How does an electric current pass through a solution (p. 74)? Why does electrolysis take place only at the electrodes and not all through the solution (p. 74)? Why is an electrovalent (polar) compound an electrolyte, while a covalent (nonpolar) compound is not (p. 204)? Why are all acids, bases, and salts electrolytes (p. 241)? Why should some hydrogen compounds, like carbonic acid (H_2CO_3), be acids, while others composed of the same elements, like alcohol (C_2H_6O), are not?

Can we fit all these facts together, make a guess about their probable relation to each other in good detective style, and show that our guess is a good one? Will our recent ideas about atomic structure help us any?

Ionization. About fifty years ago the Swedish chemist Arrhenius (Fig. 176) made a good try at putting all these facts together in what was called the *theory of ionization.* Briefly, Arrhenius supposed that in solution all electrolytes break down, or separate, or *ionize,* into two oppositely charged portions (atoms or radicals), which he called *ions.* The process of breaking down he called *ionization.* He represented the ionization of sodium chloride by the equation

$$NaCl \longrightarrow Na^+, Cl^-$$

We still use these terms much as Arrhenius used them; but we have made many changes in his theory, especially since we have found out so much about the structure of atoms. We can get a better picture of these ions and how they help to answer our questions by starting with electrovalent compounds (electrolytes).

FIG. 176. Svante August Arrhenius (1859–1927)

The great Swedish chemist who advanced the theory of ionization

Electrovalent compounds are electrolytes. We have seen that an electrovalent compound is formed by borrowing and lending electrons (p. 204), and is made up of two atoms or two groups of atoms (radicals), each having its valence orbit completed. The one got its valence orbit completed by *loss* of one or more electrons, and is therefore positively charged. *These are the positive ions*, and are given the plus (+) sign; for example, Na^+ or Ca^{++}. The other atom, or radical, has completed its valence orbit by *gain* of one or more electrons. *These are the negative ions*, and are given the minus (−) sign; for example, Cl^- or SO_4^{--}. In solution an electrolyte is parted, or ionized, into these independent ions, and it is they that carry an electric current through a solution.

Crystals of electrolytes. When and where does ionization take place? Physicists have been able to prove that in a *crystal* of an electrovalent compound these oppositely charged ions are not combined into simple molecules. They alternate with each other in the three space directions as shown in the diagram of a crystal of sodium chloride (Fig. 177). This is one of the several plans of arrangement in a crystal.

Each sodium ion has six chlorine ions around it — one on each side, one before and one behind it, one above and one below. Each chlorine ion has six sodium ions around it placed in a similar way. The whole crystal is a network — or *lattice*, as it is called — of ions arranged in this way, and held in place by electrical attraction.

A crystal of a covalent, or nonpolar, compound, on the other hand, is made up of uncharged molecules both in solution and in solid crystals.

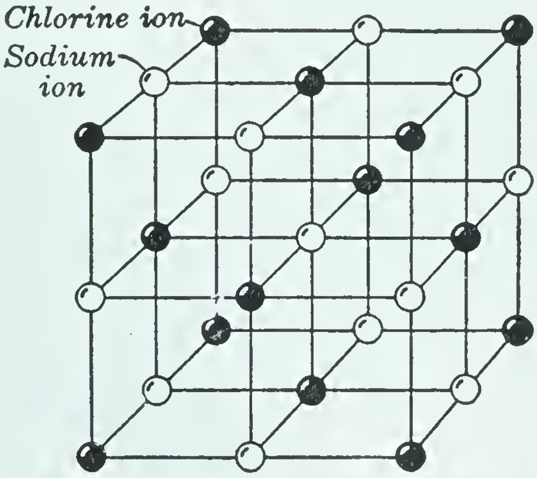


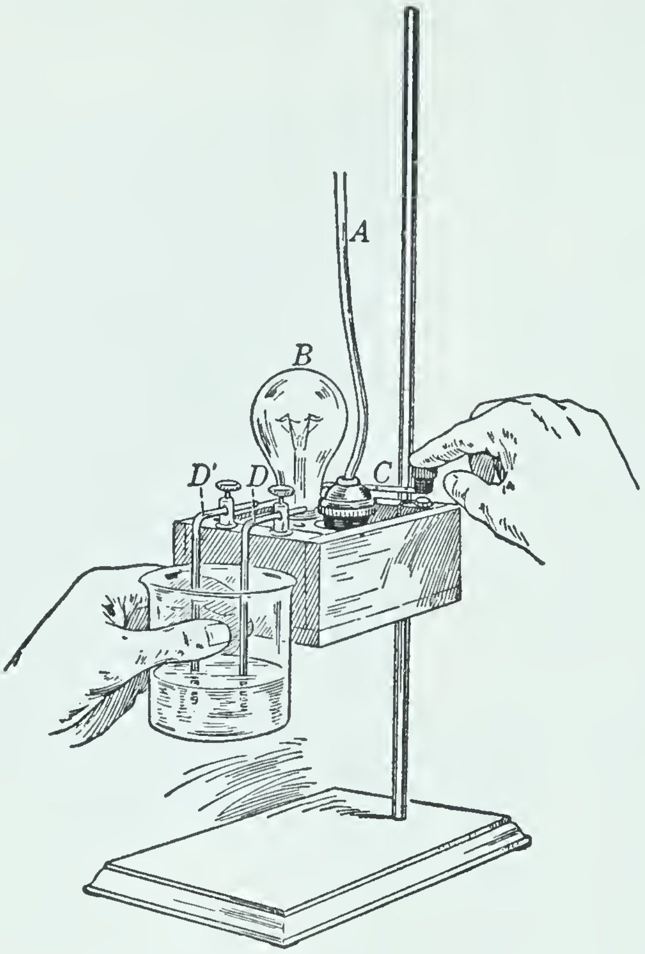
Fig. 177. Diagram of crystal lattice of sodium chloride

An electrovalent crystal dissolves into ions. When an electrovalent crystal is put into water, we can imagine that the water molecules wedge in between the ions of the crystal, pry them away one by one, and scatter them through the solution. They do not leave the crystal as *molecules* but as *ions*. So both in solution and in solid crystals an electrovalent compound is made up of ions, or is ionized. It is these charged ions that carry an electric current.

How we test the conductivity of a solution. By the *conductivity* of a solution we mean the relative ease with which it conducts the electric current — how good a conductor it is. This can be tested in a simple way, as shown in Fig. 178. The conductivity can be *measured* with great accuracy by better instruments.

Since the current is carried through a solution by the movement of the charged ions, by measuring the conductivity we can tell how many ions are present, in much the same way that from gate receipts we can tell how many people were at a game. Solutions of acids, bases, and salts are good conductors; so they have many ions. *Pure* water hardly conducts a current at all; so it has very few ions in it.

Electrolysis and ions. In Chapter XX we saw that in passing through a solution of sodium chloride an electric current produces hydrogen, chlorine, and sodium hydroxide. Do charged ions help us to account for these facts?



The path of the current is through the lamp cord *A*, the switch *C*, the lamp *B*, through the solution in the beaker from electrode *D* to *D′*, returning to the lamp cord. If the solution in the beaker is a conductor, the lamp will glow; otherwise it will not glow. The brightness of the lamp indicates the relative conductivity of the solution. The conductivity depends upon the number of ion carriers between the electrodes

FIG. 178. Testing the conductivity of a solution

Electrolysis of sodium chloride. A solution of salt contains the ions Na^+ and Cl^-, and some H^+ and OH^- from water (Fig. 179). The battery acts as an electron pump and forces some of the electrons of the atoms of the anode *B* through the wire to the cathode *A*, where they collect. So the cathode gets a negative charge and the anode a positive one.

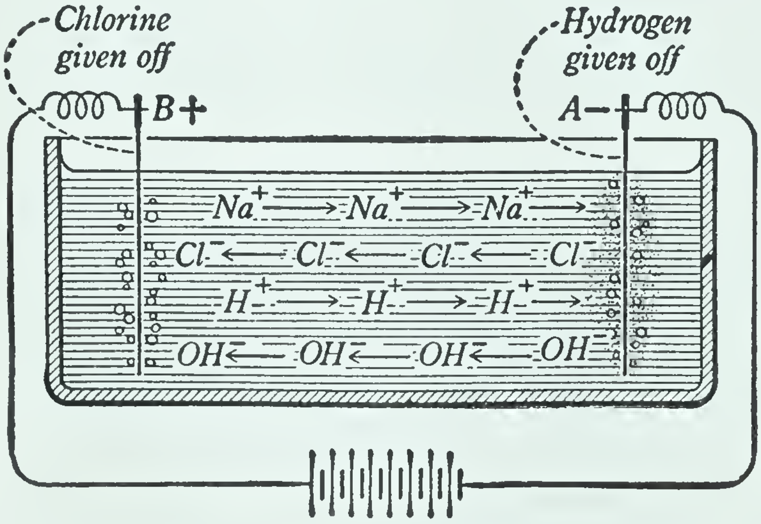


FIG. 179. A diagram illustrating the theory of the electrolysis of a solution of sodium chloride (NaCl)

The chlorine ions, each with an extra electron, are attracted to the positively charged anode *B*, to which they give up their extra electrons. They are now atoms of chlorine, and combine to form molecules of chlorine gas (which escapes at the anode). The sodium ions and the hydrogen ions, each ion lacking one of its electrons, are attracted to the cathode *A*, with its load of electrons. Both ions compete for these electrons, and the hydrogen ions win, forming atoms of hydrogen. These then unite to form molecules of hydrogen gas, which escapes from the cathode. The sodium ions and the hydroxyl ions remain in solution as Na^+, OH^-.

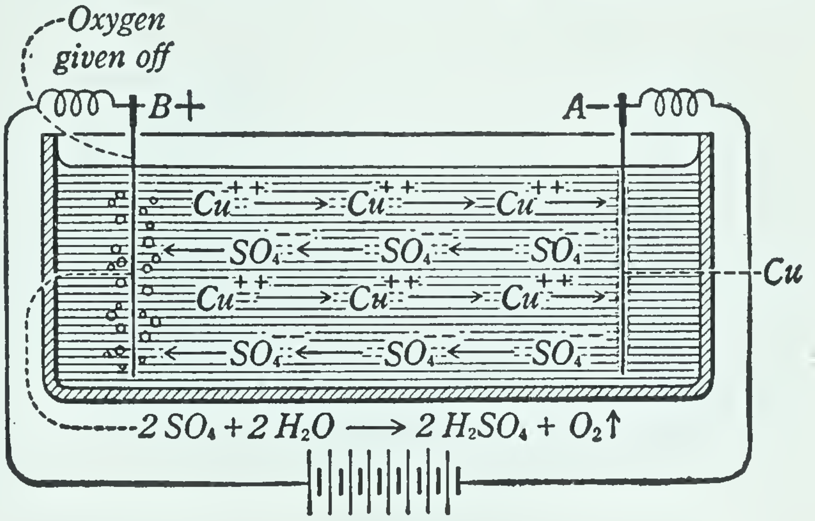

Oxygen given off
B+
A−
Cu
Cu^{++}
SO_4^{--}
$2\,SO_4 + 2\,H_2O \longrightarrow 2\,H_2SO_4 + O_2\uparrow$

Fig. 180. A diagram showing the changes that take place in the electrolysis of copper sulfate ($CuSO_4$)

In the wire nothing moves but free *electrons* — from the anode to the cathode. In solution nothing moves but *ions.*

The current does not bring about the ionization of the electrolyte, but can pass through the solution only when ions are already present.

Electrolysis of copper sulfate. If a metal ion regains electrons more easily than H^+ ions, the metal deposits on the cathode during electrolysis. For example, a solution of copper sulfate ($CuSO_4$) has the ions Cu^{++} and SO_4^{--}. The Cu^{++} ion is attracted to the (negative) cathode, *A*, gets back from it its two missing electrons, and deposits on the cathode as metallic copper (Fig. 180). It copperplates the cathode. The SO_4^{--} ion moves to the anode, *B*, and surrenders to it its two extra electrons. The uncharged SO_4 radical is very unstable and acts upon water, setting free oxygen:

$$2\,SO_4 + 2\,H_2O \longrightarrow 2\,H_2SO_4 + O_2\uparrow$$

Electrolysis of water. The reason for adding sulfuric acid to water in getting oxygen and hydrogen by electrolysis (p. 83) is now easy to explain. Pure water is very little ionized, and so conducts an electric current very poorly.

Sulfuric acid is an electrolyte, and in water gives the ions 2 H^+ and SO_4^{--}. During the electrolysis of the solution the H^+ ions travel to the cathode, *A* (negative), recover their lost electrons from it, and, as hydrogen atoms, combine to form molecules of hydrogen gas (Fig. 181). The SO_4^{--} ions move to the anode, *B* (positive), and surrender their extra electrons to it; and the uncharged group SO_4 then acts upon water, setting free oxygen as shown in the last paragraph. This process can go on as long as any water is left. So the hydrogen and oxygen come either directly or indirectly from the water, and in the proportion in which they are present in it.

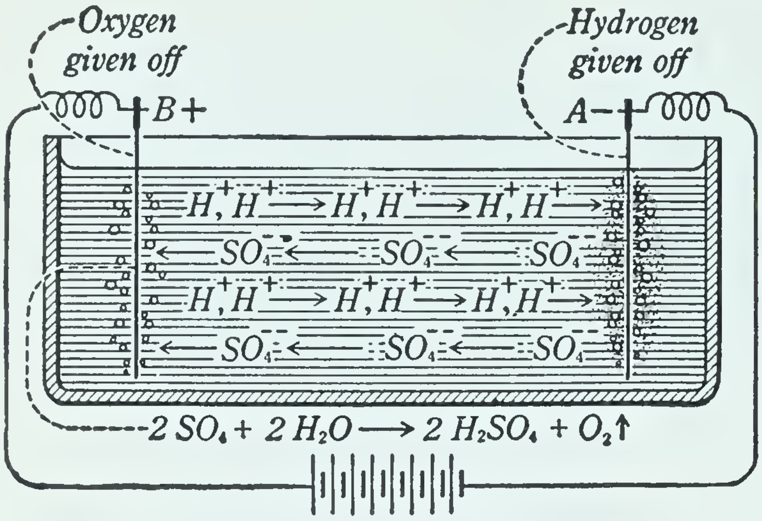

Oxygen given off
Hydrogen given off
B+
A−
$H^+, H^+ \rightarrow H^+, H^+ \rightarrow H^+, H^+ \rightarrow$
$SO_4^{--} \leftarrow SO_4^{--} \leftarrow SO_4^{--}$
$2\ SO_4 + 2\ H_2O \rightarrow 2\ H_2SO_4 + O_2\uparrow$

FIG. 181. A diagram showing the changes that take place in the electrolysis of water

All electrolysis takes place at the electrodes. From the three examples just given it will be clear why there is no sign of chemical action (electrolysis) *anywhere in the solution,* but only at the surface of the electrodes. This is where the ions give up or recover electrons and become uncharged, or normal, atoms or radicals. They are then free to act as chemical elements or very unstable compounds.

The positively charged ions that are attracted to the (negative) cathode are called *cations*. The negatively charged ions that are attracted to the (positive) anode are called *anions*.

Electrolytes vary in conductivity. If we weigh out a gram-molecular weight of sodium chloride (58.454 g) and dissolve it in a liter of water, the 58.454 g of NaCl should give 22.997 g of Na^+ ions and 35.457 g of Cl^- ions. From these figures we can calculate what the conductivity of the solution should be. But by actual *experiments* we find it is *less* than the value given by calculation.

In similar solutions of other salts, strong acids, and strong bases the conductivity is never more than about 75–80 per cent of the calculated value, and with weak acids and bases it is very much less — even less than 1 per cent.

We must accept it as a *fact* that electrolytes differ widely among themselves in their conductivity in solutions of equal concentration. We speak of the percentage of expected conductivity as the *degree* or *extent of ionization* of an electrolyte.

The degree of ionization depends on a number of things. Among these are (1) the nature of the electrolyte; (2) the solvent (in equal concentrations the degree of ionization of an electrolyte is different in each solvent in which it is soluble); (3) the concentration (the more dilute the solution the greater is the percentage of ions taking part in conductivity).

Free and bound ions. Our explanation of electrolysis does not help us to understand *why* some of the ions in a solution fail to do their part in conducting the current. We simply know it to be a fact. For want of a better name we call them *bound* ions. Many guesses have been made as to why some ions should be inactive; but none are easy to describe, and none are entirely satisfactory. We shall simply accept it as a fact that in the solution of any electrolyte a certain percentage of its ions are *free*, or *active*, and others are *bound*, or *inactive*. At a given concentration of an electrolyte *the percentage of its ions that are free* is its degree, or extent, of ionization.

How shall we represent bound ions? We have seen that in a solution of an electrolyte the free ions are in equilibrium with the bound ions. Chemists are agreed upon a method for representing the free ions, but not for representing the bound ions. For our purposes we may draw a line above the symbols of the bound ions, and express the equilibrium, say in the case of sodium chloride, as follows:

$$\underset{\text{bound ions}}{\overline{\text{Na}^+, \text{Cl}^-}} \rightleftharpoons \underset{\text{free ions}}{\text{Na}^+, \text{Cl}^-}$$

The double arrows mean that the percentages of the free and the bound ions are easily changed. If the solution is diluted, the percentage of free ions increases; if it is concentrated by evaporation, the percentage of bound ions increases.

Acids, bases, and salts. In Chapter XXI brief descriptions were given of these three classes of compounds, along with definitions for each class, based mainly upon their properties. Since they are all electrolytes, and since we have now seen what happens when they are dissolved in water, it will be of interest to define each class from the standpoint of the ionization theory.

Acids and ionization. Hydrogen forms both electrovalent and covalent compounds with other elements. The covalent compounds, of which alcohol (C_2H_6O) is an example, have no acid properties. The electrovalent compounds (HCl, H_2SO_4) are all acids. In water solution the electrovalent hydrogen is a positive ion, and this is the one thing all acids have in common. So, from the standpoint of the ionization theory, we have the following definition:

An acid is an electrovalent compound that gives positive hydrogen ions (cations) in water solution.

The strongest acids are those that have the largest percentage of ionization at a given concentration.

$$\overline{H^+, Cl^-} \rightleftarrows H^+, Cl^-$$

$$\overline{H^+, H^+, SO_4^{--}} \rightleftarrows H^+, H^+, SO_4^{--}$$

Bases and ionization. Many compounds contain the hydroxyl radical (OH). Some of these are covalent compounds and have no basic properties. Others are electrovalent compounds in which the negative hydroxyl group, or ion (OH^-), is one of the parts, the other being a positive metal ion. The hydroxyl ion is the one thing which all bases have in common, and which gives them basic properties. So, from the standpoint of the ionization theory, we have this definition:

A base is an electrovalent compound that gives negative hydroxyl ions (anions) in water solution.

$$\overline{Na^+, OH^-} \rightleftarrows Na^+, OH^-$$

Neutralization and ionization. Experiment proves that water is a very poor conductor of electricity. This is simply another way of saying that it is very little ionized. We can turn this statement around and say that only in very small concentration can H^+ ions and OH^- ions exist together (in solution). Most of them unite to form water:

$$H^+ + OH^- \longrightarrow H_2O$$

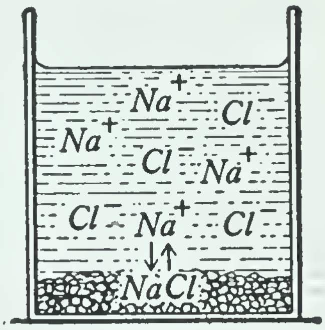


FIG. 182. Ions of sodium chloride building crystals of the solid salt

So when we bring an acid and a base together in solution, the H^+ ions of the acid and the OH^- ions of the base disappear, and with them all acid and basic properties:

$$H^+,\ Cl^- + Na^+,\ OH^- \longrightarrow Na^+,\ Cl^- + H_2O$$

$$H^+,\ H^+,\ SO_4^{--} + 2\,(Na^+,\ OH^-) \longrightarrow Na^+,\ Na^+,\ SO_4^{--} + 2\,H_2O$$

In all such cases we say that the acid and the base *neutralize* each other. From the standpoint of the ionization theory,

Neutralization is the union of equal numbers of the hydrogen ions of an acid and the hydroxyl ions of a base to form water.

Salts and ionization. In the equations of the last paragraph it will be seen that after neutralization the positive metal ions of the base and the negative ions of the acid are left in the solution in equivalent numbers. These are the ions of a salt, and from a concentrated solution they build up crystals of the solid salt (Fig. 182). So we may say that from the standpoint of the ionization theory,

A salt is an electrovalent compound made up of the positively charged ion (cation) of a base and the negatively charged ion (anion) of an acid.

Strength of acids and bases. Since acid and basic properties are due to hydrogen ions and hydroxyl ions, respectively, those acids or bases which give the greatest percentage of active ions at a given concentration are the strongest ones. The acids and bases described in the foregoing paragraphs are all quite strong. In 10 per cent solutions about half of the ions are active, and this is also approximately true of most salts at this same concentration. Solutions of weak acids and bases have a smaller percentage of active ions.

Electrolysis of a melted salt. It is not surprising to find that a *melted* salt is often a good electrolyte. This is an important fact in many industrial processes, as in the production of sodium (p. 233). As we heat a crystal we make the ions of which it is composed vibrate more and more in their places until finally the vibration is great enough to overcome the electrical attraction that holds the ions in place. They begin to move about *at random*, like a regiment of soldiers when they hear the order "break ranks," and are as free to carry a current as they are in a solution.

A word about equations. If in an equation we wish to call attention to the part played by the ions, we write it in ionic form:

$$H^+, NO_3^- + K^+, OH^- \longrightarrow K^+, NO_3^- + H_2O$$

If we simply want to show the substances taking part in a reaction and the final products formed, we write the equation in molecular form:

$$HNO_3 + KOH \longrightarrow KNO_3 + H_2O$$

We shall use both forms in the remaining chapters.

Electromotive (or electrochemical) series. When a piece of zinc is put into an acid, zinc passes into solution, and hydrogen is set free:

$$Zn + 2\ HCl \longrightarrow ZnCl_2 + H_2\uparrow$$

or

$$Zn + 2\ H^+, Cl^- \longrightarrow Zn^{++}, Cl^-_2 + H_2\uparrow$$

In like manner, when zinc is placed in a solution of a salt of copper, such as the sulfate, $CuSO_4$, zinc passes into solution, and a corresponding quantity of copper is precipitated:

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$

or

$$Zn + Cu^{++}, SO_4^{--} \longrightarrow Zn^{++}, SO_4^{--} + Cu$$

It will be seen that the anions Cl^- and SO_4^{--} take no part in the reaction, since they appear on both sides of the equation. The important fact in the reaction is that in each case the zinc atoms give up two electrons, in the first case to hydrogen ions and in the second case to copper ions; so the equations might be written

$$Zn + 2\ H^+ \longrightarrow Zn^{++} + H_2$$

and

$$Zn + Cu^{++} \longrightarrow Zn^{++} + Cu$$

Copper ions and hydrogen ions can both recover their lost electrons from zinc atoms. On the other hand, copper has no effect upon a solution of zinc sulfate.

It is possible to arrange hydrogen and the metals in a table in such a way that any element in the list will displace any one *below* it from its salts and will, in turn, be displaced from its salts by any one *above* it. This list is called the *electromotive series* (or the *electrochemical series*).

ELECTROMOTIVE SERIES

1. Lithium
2. Potassium
3. Calcium
4. Sodium
5. Magnesium
6. Aluminum
7. Manganese
8. Zinc
9. Chromium
10. Iron
11. Cadmium
12. Cobalt
13. Nickel
14. Lead
15. Tin
16. **Hydrogen**
17. Copper
18. Arsenic, antimony, bismuth
19. Mercury
20. Silver
21. Platinum
22. Gold

With this table we can foretell many reactions. For example, from the positions of the two metals we should expect magnesium to displace tin from its salts; and so it does:

$$Mg + Sn^{++}, Cl^{-}{}_2 \longrightarrow Mg^{++}, Cl^{-}{}_2 + Sn$$

We should not, however, expect iron to displace aluminum; and it does not.

It is of especial interest to notice the position of hydrogen in the series. All the metals above it will evolve hydrogen from acids, while those below it will not. In the latter case, if any action takes place, it is preceded by oxidation.

It will be recalled that sodium liberates hydrogen from water as well as from acids. All the metals above hydrogen do this, though in many cases the action is very slow.

A different view of acids and bases. It is very unlikely that a free proton (H^+) exists as such in water (or in other solvents), but almost certain that it combines with the solvent molecules. With water this gives the compound ion H_3O^+, called the *hydronium ion.* It is formed as follows:

$$H^+, Cl^- + H_2O \longrightarrow H_3O^+ + Cl^-$$

This view (of Brönsted) leads to new definitions for acids and bases: An acid is any molecule or ion that gives up a proton (H^+) in solution; a base is any molecule or ion that takes up a proton in solution. Water, ammonia, and the ions OH^- and CO_3^{--} are *bases*; while our hydrogen acids are still acids, their anions are bases of varying strength. Those interested in this new view should consult Appendix F.

CHAPTER SUMMARY IN QUESTION FORM

1. What name is given to a compound whose solution in water (*a*) conducts the electric current? (*b*) does not conduct the electric current?

2. Give an example of a liquid that is (*a*) a conductor; (*b*) a nonconductor.

3. Is the passage of a current through a liquid accompanied by (*a*) a physical change or (*b*) a chemical change or (*c*) neither?

4. What is meant by the word *electrolysis*?

5. What groups of compounds are all electrolytes?

6. (*a*) Who formed a theory to account for the facts of electrolysis? (*b*) What is the theory called?

7. Give the essential parts of the theory of ionization, and illustrate by reference to what happens when sodium chloride is dissolved in water.

8. What is meant by (*a*) free ions? (*b*) bound ions? (*c*) In an equation how do you represent the difference between them?

9. Write an equation which expresses the fact that in a solution of sodium chloride a state of equilibrium exists between free and bound ions.

10. By the use of the equation in question 9, how could we overcome the equilibrium (*a*) so as to increase the number of free ions of sodium chloride present? (*b*) so as to increase the number of bound ions present?

11. From the list given below select the word or phrase to which the following descriptions apply: (*a*) found in all acids; (*b*) found in all bases; (*c*) the positive part of an ionized compound; (*d*) the negative part of an ionized compound; (*e*) contains hydrogen ions; (*f*) contains anions from the acid and cations from the base; (*g*) is the union of the hydrogen ions of the acid and the hydroxyl ions of the base; (*h*) the electrode where there is an excess of electrons; (*i*) the electrode where there is a deficiency of electrons.

Cathode
Ions
Anion
Cation
Hydrogen ions
Hydroxyl ions
Acid
Base
Salt
Neutralization
Anode

12. Some sodium chloride is dissolved in water, and a current of electricity is passed through the solution. Are ions of the salt already present, or not until the current is passed through the solution?

13. Explain what is meant by the following words or phrases, in terms of the theory of ionization: (*a*) acid; (*b*) base; (*c*) salt; (*d*) neutralization; (*e*) strong acid; (*f*) weak base.

14. Show how the theory of ionization accounts for the fact that pure hydrogen chloride will not change blue litmus red, but its solution in water will produce this change.

15. Name the products formed when a current of electricity is passed through a solution of each of the following compounds: (*a*) sodium chloride; (*b*) copper sulfate; (*c*) water containing a small percentage of sulfuric acid. (*d*) Show how the theory of ionization accounts for the formation of the products in each case.

16. What is (*a*) a cation? (*b*) an anion?

17. Write two forms of an equation expressing the reaction between hydrochloric acid and sodium hydroxide in solution, to represent (*a*) the details of the reaction (ionic equation); (*b*) the final products only.

18. What names are given to the grouping of hydrogen and the metals in such a way that any element in the list will replace any one below it from solutions of its salts?

THOUGHT QUESTIONS

1. (*a*) Do the ions of an element have the same properties as their atoms? (*b*) Illustrate in the case of sodium and chlorine.

2. Account for the presence of sodium hydroxide in a solution of sodium chloride through which a current of electricity is passing.

3. From the standpoint of the theory of ionization, write the equations for the following reactions: (*a*) nitric acid and sodium hydroxide; (*b*) sulfuric acid and sodium hydroxide; (*c*) hydrochloric acid and calcium hydroxide.

4. Predict what would happen if a strip of copper were placed in a solution (*a*) of silver nitrate; (*b*) of zinc sulfate; if a strip of zinc were placed in a solution (*c*) of silver nitrate; (*d*) of copper sulfate.

5. In general, should you expect a metal that liberates hydrogen from water to liberate hydrogen from acids also?

6. Where in the electromotive series should you expect to find those elements that are found free in nature?

OPTIONAL EXERCISES

1. Write a theme on "The Value of Theories," illustrating your statements by reference to the theory of ionization.

2. From the standpoint of the theory of ionization, predict what would happen if you were to pass a current of electricity through (*a*) a solution of potassium chloride; (*b*) a solution of sodium sulfate; (*c*) a solution of potassium sulfate.

UNIT READINGS

BEERY. *Stuff.* [Read about chlorine, pp. 60–72, and about sodium and potassium, pp. 321–337.]

CLARKE. *Marvels of Modern Chemistry.* [Chapter XVI treats of the alkali metals. These include sodium and potassium. Chapter VII tells of Arrhenius and the theory of ionization.]

FRENCH. *The Drama of Chemistry.* [Chapter V gives a good account of the theory of ions.]

HOLMYARD. *Chemistry for Beginners.* [Chapter VIII gives a simple account of acids, bases, and salts.]

JAFFE. *Crucibles.* [Chapter XII tells about Arrhenius, who was the first to advance the theory of ionization.]

WEEKS. *The Discovery of the Elements.* [Read about the discovery of chlorine, pp. 253–257; also about the discovery of sodium and potassium, pp. 117–124.]

The Chemistry Leaflet. [No. 4 of recent volumes contains information about chlorine; No. 5, about acids, bases, and salts; No. 18, about sodium and potassium.]

Unit Six. Some Inactive Elements and How They Serve Us: a Unit of Many Contrasts

THIS unit deals with a wide variety of interesting gases, brought together here for study by the one idea that they act very slowly or not at all. The air we breathe is a mixture of such gases. Suppose the oxygen, nitrogen, and water vapor in it did act together easily. The earth would be drenched with nitric acid.

We must have oxygen in our lungs, and it must be active chemically; but we have to rely on a wonderful catalyst (the red matter of the blood cells) to bring about this activity. With this catalyst the temperature of our bodies in health is kept at about 98° F. We must build up nitrogen into the body structure, but we are helpless to take any of it from the wealth of nitrogen that constantly fills our lungs. We have to rely on plants to prepare our nitrogen food; and they, in turn, have to depend on humble bacteria.

Some of the gases in the atmosphere will not act at all on anything. They are among the rarest elements on earth; yet every town in the country blazes nightly with red neon signs.

When with great care we build up nitrogen compounds, we find that they tend to go to pieces suddenly, like a house of cards. They are our high explosives. Yet many of the reactions of simple nitrogen compounds take place with such reluctance that they do not seem to care which way they go, and even go both ways at the same time.

It is a unit that touches our lives very closely, and will lead us to some new chemical ideas.

CHAPTER XXIII

Nitrogen and Some Rare Gases

[Gases That Act with Difficulty or Not at All]

A chapter by way of contrast. The elements we have so far studied are all very active, at least at moderately high temperatures. Hydrogen, oxygen, chlorine, sodium, and potassium all either lack one or two electrons in their valence orbit and are eager to capture the missing ones, or have one or two that they would be glad to get rid of so as to be left with their outer orbit completed.

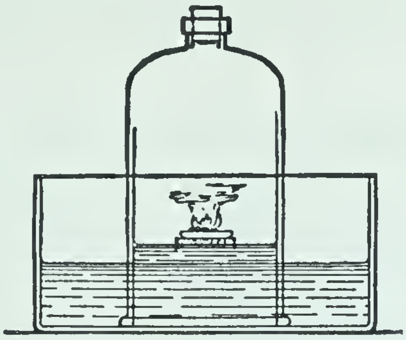
The elements we shall now study are very inactive. If we take extreme measures with nitrogen, we can, much against its will, compel it to unite directly with other elements and so to form compounds. The remaining elements of the chapter refuse to have anything to do with other elements, and so, with one or two exceptions, form no compounds. Even the atoms of the same element (nitrogen excepted) will not unite as do the atoms of all other gaseous elements. It is a very lazy group we have got together.

NITROGEN

We ought to be well acquainted with nitrogen. In every 100 volumes of *dry* air there are about 78 volumes of nitrogen gas; so all the time we have about four times as much nitrogen in our lungs as oxygen. We live at the bottom of a deep sea of nitrogen diluted with other gases. Nitrogen compounds (those called proteins) are an essential part of our food, and a person of average weight (150 lb) carries around as part of *himself* about 4.5 lb of nitrogen.

As a mineral, nitrogen is found in a few places as the salts potassium nitrate, or *saltpeter* (KNO_3), and sodium nitrate ($NaNO_3$), or *Chile saltpeter*. In some kind of combination it is present in all fertile soils, or they would not *be* fertile.

Who discovered nitrogen? Nitrogen was first recognized as an individual gas by a young Scottish boy named Daniel Rutherford, who later became the uncle of Sir Walter Scott.



A small piece of phosphorus is placed on a crucible lid supported by a cork floating on water. The phosphorus is ignited and a bell jar (or bottle) quickly placed over the cork as shown in the figure. The phosphorus unites with the oxygen present in the air trapped in the jar, forming a white oxide which soon dissolves in the water, thus leaving the nitrogen

FIG. 183. Preparing nitrogen by burning phosphorus in air

This important discovery was announced as he graduated from his medical course in 1772. He did no further chemical work, but was a doctor and a professor of botany.

What nitrogen is like. Nitrogen is a colorless gas. The air has no color to our eyes. Nor has nitrogen taste or odor. It is about as insoluble in water as is oxygen or hydrogen. At very low temperatures and under great pressure it condenses to a colorless liquid which boils at − 195.8° and freezes at − 209.8°, forming crystals that look like ice.

Preparation of nitrogen. On a large scale nitrogen is always prepared from liquid air, as will be described in the following chapter. In the laboratory it is got by one of two methods:

The preparation of nitrogen from air. Oxygen is very much more active than nitrogen. So it is possible to get nitrogen by passing air over some substance that will form an oxide with the oxygen, leaving the nitrogen unchanged. The oxide formed must be a liquid or a solid, so that it can be separated easily from the nitrogen gas.

Phosphorus is sometimes used for this purpose (Fig. 183), because it has a strong affinity for oxygen; but phosphorus is a dangerous substance to work with. More often copper is used. When air is passed through a tube filled with hot copper gauze (so as to get a large surface), the oxygen in the air combines with the copper to form copper oxide (CuO), a black solid, which stays in the tube, while the nitrogen passes on and is collected (Fig. 184).

The preparation of nitrogen from compounds of nitrogen. Nitrogen from air is never entirely pure. Small percentages of the rare elements helium, argon, neon, krypton, and xenon, originally present in the air, are always mixed with it. These rare gases make up only about 1 per cent of the nitrogen, and they resemble nitrogen in most respects; so they do not greatly change its properties.

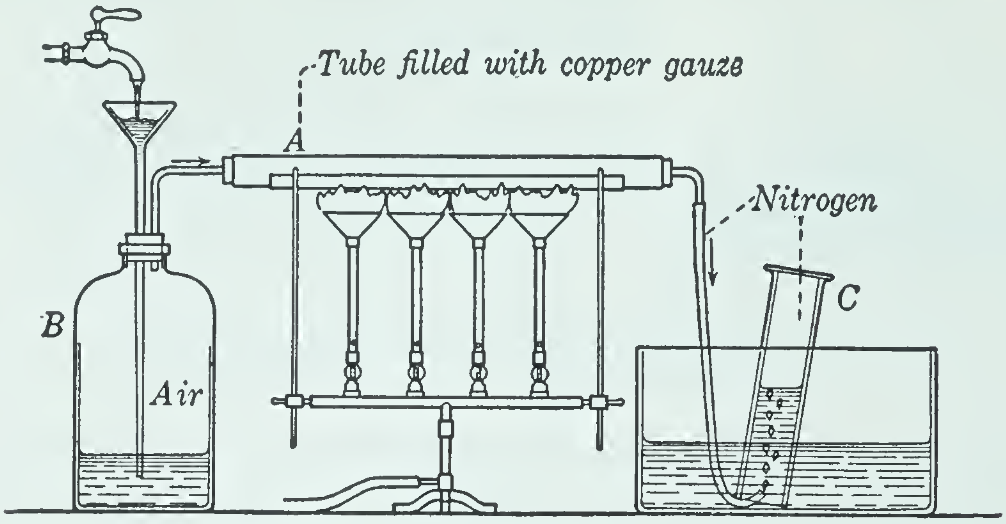


FIG. 184. Preparing nitrogen from air with hot copper

Air from the bottle *B* is forced over hot copper in the tube *A* by pouring water into the funnel. The copper removes the oxygen, and the nitrogen collects in *C*

Perfectly pure nitrogen may be obtained by decomposing some of its compounds. Nitrogen has so little affinity for most elements that with little urging it leaves many of its compounds and goes off by itself as a gas. Ammonium nitrite (NH_4NO_2) is often used in preparing nitrogen. When this is heated it decomposes into water and nitrogen:

$$NH_4NO_2 \longrightarrow 2\,H_2O + N_2\uparrow$$

Nitrogen is very inactive. The fact that there is so much free nitrogen in the air, and that there are so few of its mineral compounds on earth, shows how inactive the element is even at rather high temperatures.

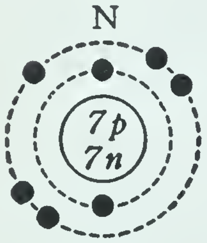


FIG. 185. The nitrogen atom

Nitrogen has five electrons in its valence orbit (Fig. 185) and needs three more to complete it. So we should expect it to borrow from hydrogen and from such metals as sodium and calcium, which are very ready to lend. With elements like oxygen it would have to form covalent compounds.

We find that nitrogen does combine with hydrogen to form *ammonia* (NH_3) and with many of the metals to form *nitrides*, such as aluminum nitride (AlN). Even then it is often necessary to use a catalyst or to work at moderately high temperatures and pressures. At very high temperatures, as in an electric arc or in the path of an electric spark or lightning flash, nitrogen combines with oxygen (Fig. 186). But the reaction, once started, does not continue as it does when hydrogen starts to combine with oxygen or with chlorine.

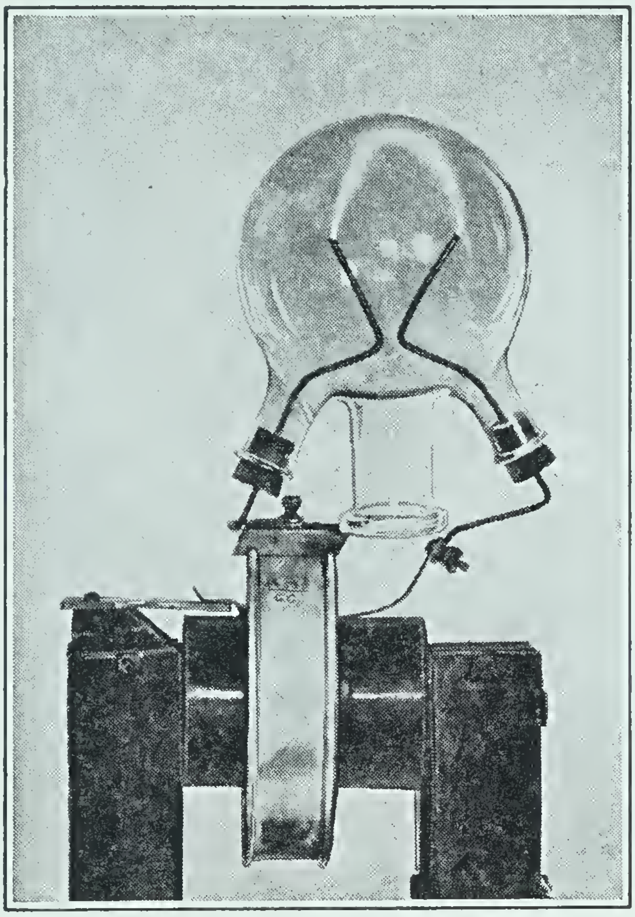


FIG. 186. Combining nitrogen and oxygen

The nitrogen and oxygen in the air of the flask combine when an electric discharge is passed through it

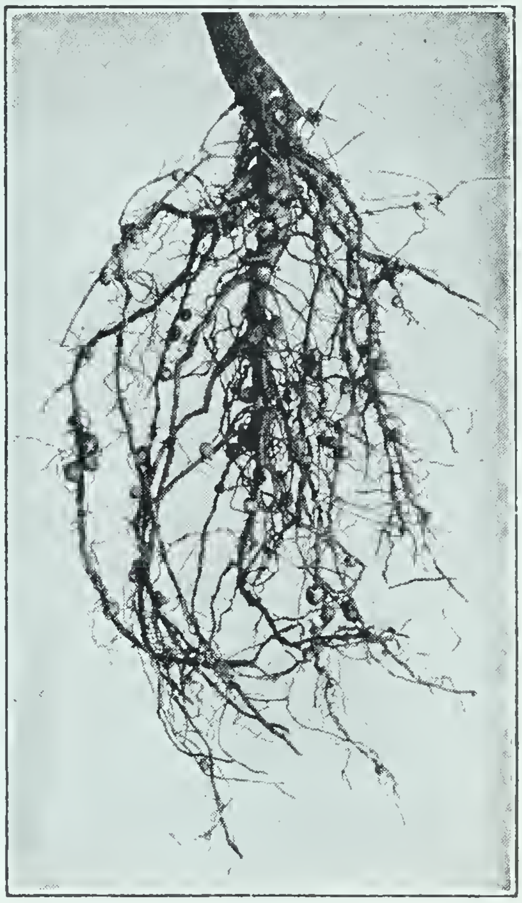


FIG. 187. Nodules on the roots of a soy-bean plant

These nodules are the homes of myriads of bacteria

Uses of nitrogen. The chief use of nitrogen in industry is in the preparation of ammonia (NH_3), which is the first step in the manufacture of important fertilizers and of nitric acid (HNO_3). Smaller amounts are used in the manufacture of calcium cyanamide (p. 535), which is also used as a fertilizer. Many electric-light bulbs are partly filled with the gas.

The fixation of nitrogen by plants. Nitrogen is a necessary part of all living things, both plant and animal. Yet few of them can take *free* nitrogen from the air and build it into their own living structure. They must get their nitrogen food from

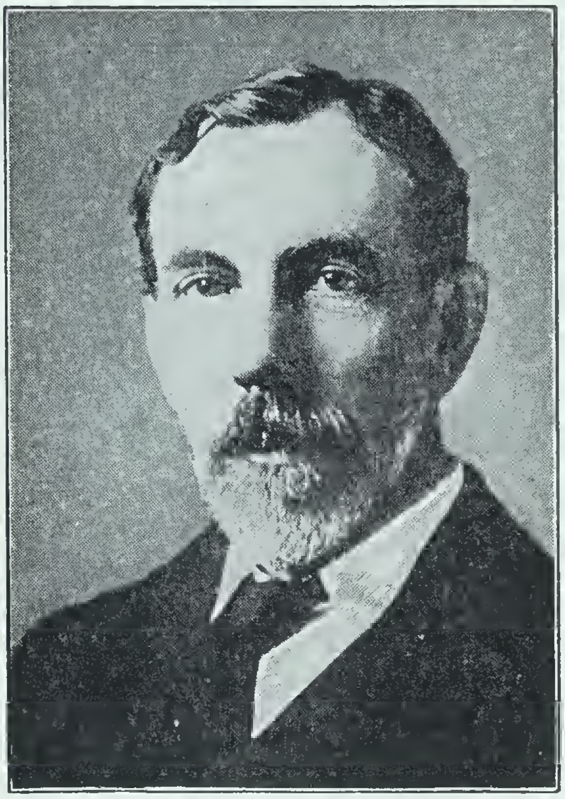


Fig. 188. Sir William Ramsay (1852–1916)

A Scottish chemist, who, together with the English scientist Lord Rayleigh, discovered argon. In association with Travers he also discovered the elements xenon, neon, and krypton and was the first to show that helium exists on the earth. For these and other outstanding discoveries, Ramsay was awarded the Nobel prize in 1904

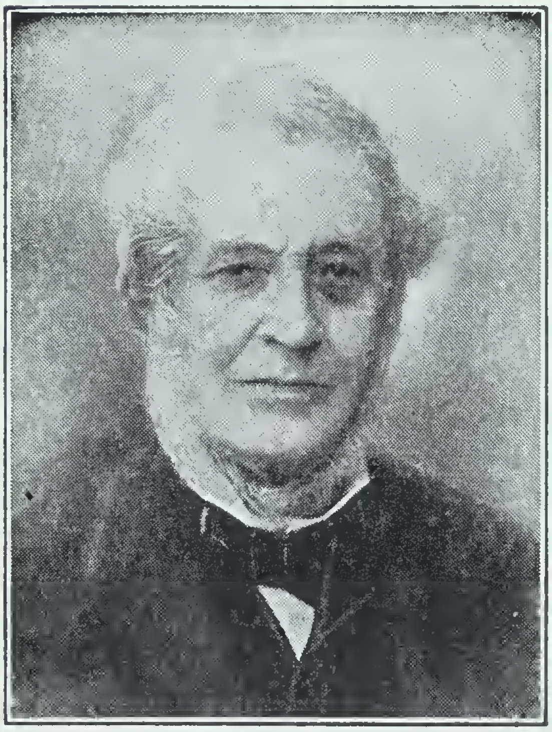
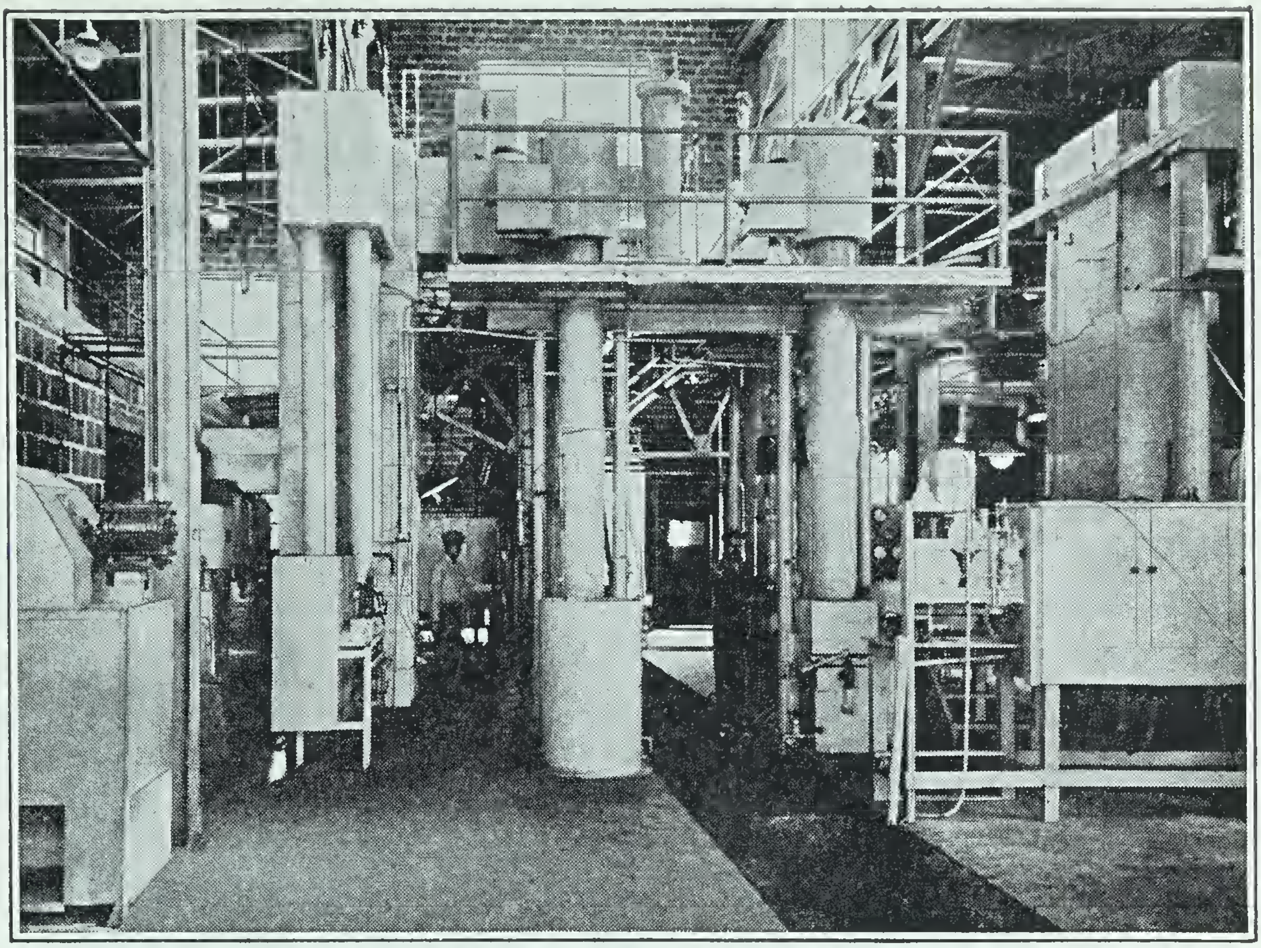


Fig. 189. Robert Wilhelm Bunsen (1811–1899)

A distinguished German chemist. Bunsen discovered rubidium and cesium by means of the spectroscope, an instrument devised by Bunsen and Kirchhoff. Bunsen also devised a filter pump, a galvanic cell, a laboratory gas burner (Bunsen burner), and other useful apparatus. He worked out a method for preparing magnesium on a large scale and contributed much to our methods for analyzing gases



United States Bureau of Mines

Fig. 190. View in a plant in Texas for the preparation of helium

The natural gas that contains a small percentage of helium is subjected to great pressure and cooling. Under these conditions all the gases present are liquefied except helium, and so the helium can be separated in a pure state

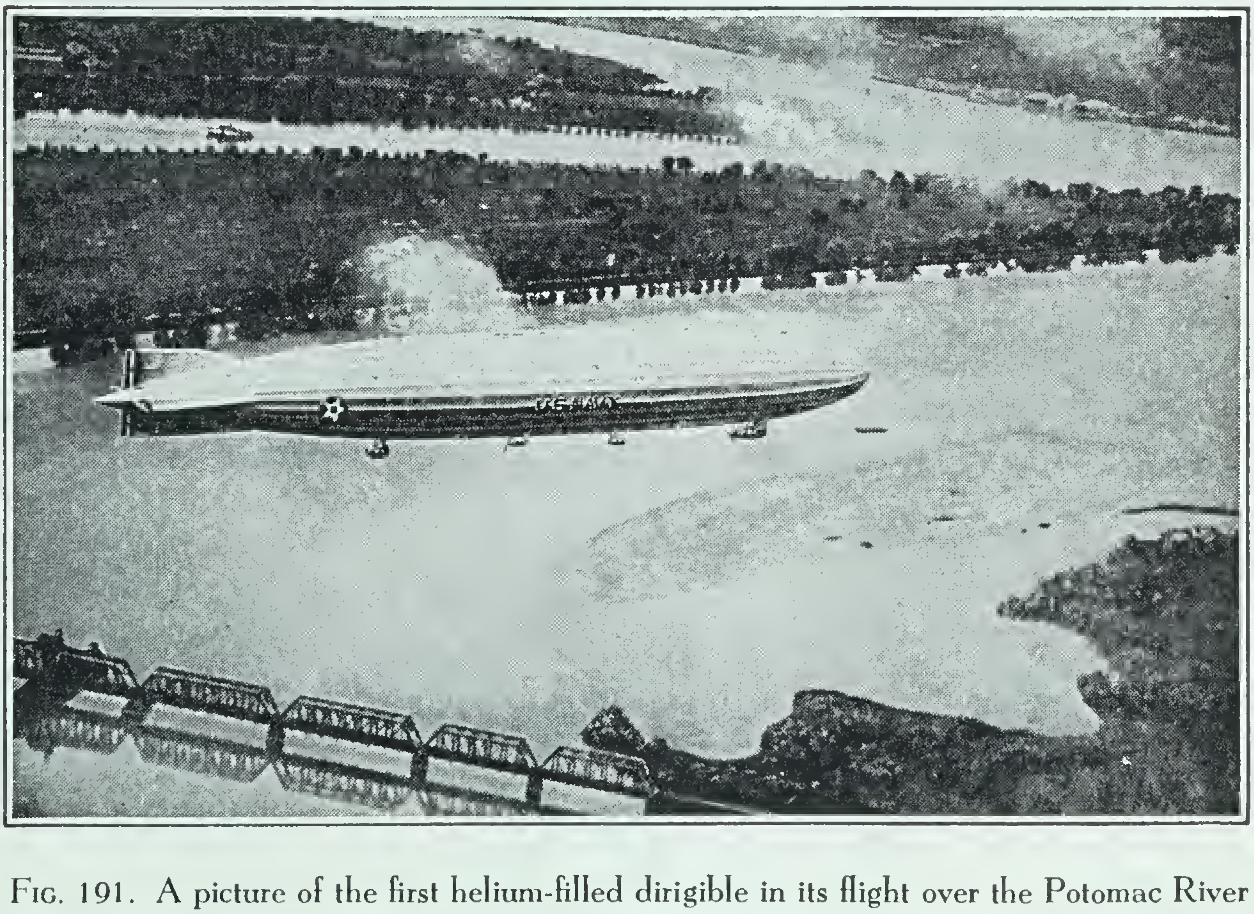


Fig. 191. A picture of the first helium-filled dirigible in its flight over the Potomac River at Washington, D. C., December, 1921

compounds of nitrogen, and these are not abundant, either in the air or in the soil. Where does the supply come from?

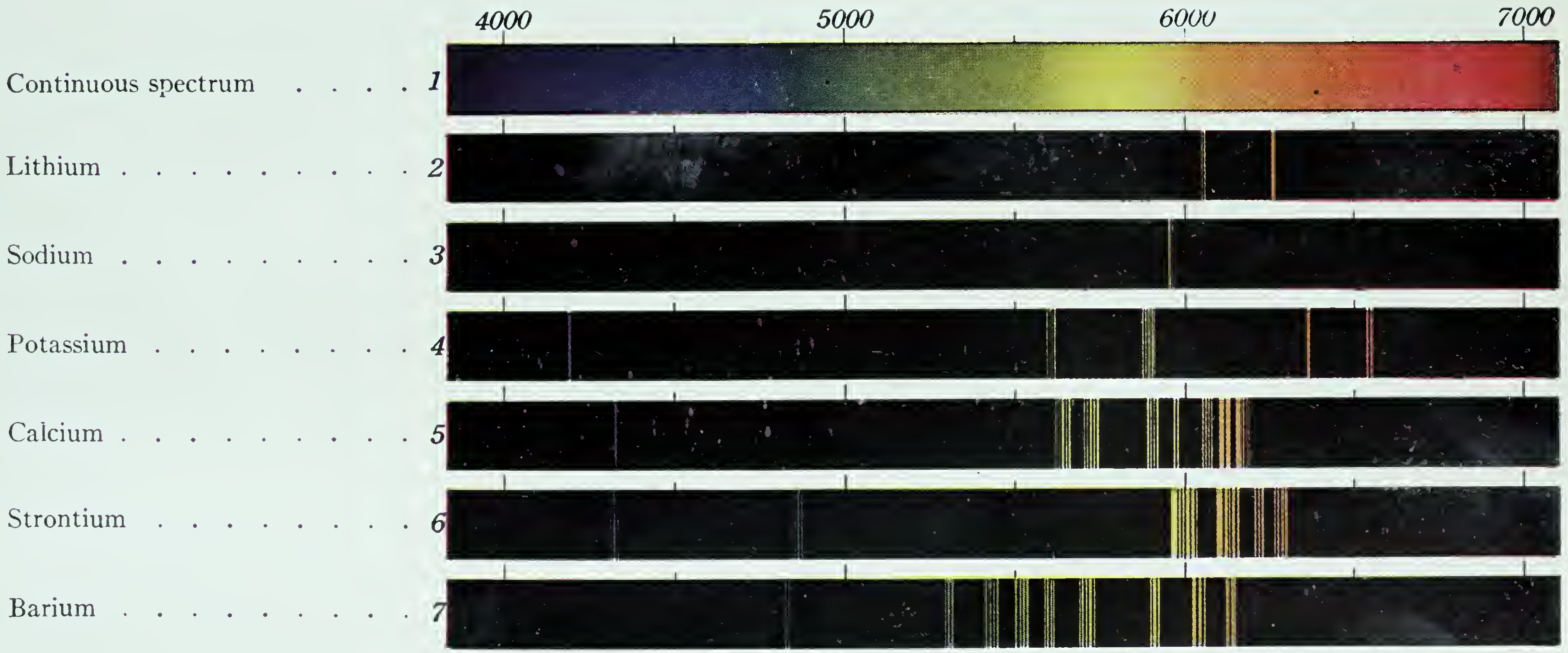
Farmers have long known that crops of clover, peas, beans, and similar plants improve the soil, and more recently scientists have shown *why* this is so. On the roots of these plants are little *nodules* that look like minute potatoes on the roots of a potato plant (Fig. 187). In reality these are the homes of swarms of bacteria that in some way bring about the combination of free nitrogen from the air with other elements (chiefly oxygen). The compounds so formed are in part built into the growing plant above the nodules, and in part dissolve into the soil and provide food for other plants. This process is called *fixation of nitrogen* — in this case brought about by the so-called *nitrifying* bacteria.

THE "LAZY" ELEMENTS OF THE ATMOSPHERE

A bit of history. For centuries chemists had studied the atmosphere, and they thought they knew all about its composition. Great was their surprise, about forty years ago, when the Scottish chemist Ramsay (Fig. 188) and his associates discovered five new gaseous elements in the atmosphere in minute percentages. These elements are helium, neon, argon, krypton, and xenon. They are all colorless, odorless gases, and are very strange elements because *their atoms do not combine with each other to form molecules of the element, nor with atoms of other elements to form molecules of compounds* (except in a few instances under extreme conditions). With these gases (p. 181), 22.4 liters contain 1 *gram-atom* of the element, not 1 gram-molecule. The valence orbits of their atoms are completely filled — that of helium, with 2 electrons; the others, with 8.

Table of the Inactive Gases

Name	Electrons in Each Orbit	Volume in 10,000 of Air
Helium	2 (See Fig. 121)	0.04
Neon	2 : 8 (See Fig. 129)	0.18
Argon	2 : 8 : 8 (See Fig. 133)	94.00
Krypton	2 : 8 : 18 : 8	0.01
Xenon	2 : 8 : 18 : 18 : 8	0.0009


4000
5000
6000
7000
Continuous spectrum 1
Lithium 2
Sodium 3
Potassium 4
Calcium 5
Strontium 6
Barium 7

A CONTINUOUS SPECTRUM AND SIX BRIGHT-LINE SPECTRA

These seven colored bands are typical of the many that may be seen in the spectroscope. Number 1, called a *continuous* spectrum, is an unbroken gradation of colors ranging from violet to red, and is seen when a spectroscope is directed at a solid body heated to incandescence. The others are *bright-line* spectra and are examples of what is seen in the spectroscope when various elements (or their compounds) are vaporized in a Bunsen flame or in an electric arc, each spectrum being characteristic of some one element. The numbers at the top refer to the wave lengths of light, measured in suitable units

In describing the structure of the atom, we did not go beyond any atoms that had more than 18 electrons, the number present in the argon atom (p. 174). In all these the first orbit never contains more than 2 electrons, the second never more than 8; and the third, never more than 8. With atoms that contain more than 18 electrons we often find a larger number present in some of the orbits. For example, the krypton atom contains 18 electrons in the third orbit, while both the third and the fourth orbit of xenon contain 18 electrons, as given in the table on page 270.

The discovery and source of helium. Helium has the great distinction of having been discovered on the sun long before anyone was able to find it on the earth. It was discovered by the use of the spectroscope (Fig. 193), which enables us to tell just what elements are present in any very hot gas or vapor. So far as we know, the American chemist Hillebrand was the first who actually obtained helium, although he did not know that he had it. He found that when certain rare minerals are heated, a gas is given off. He tested this gas and concluded that it was nitrogen. A few years later the Scottish chemist Ramsay (Fig. 188), repeated Hillebrand's experiments and found that the gas given off on heating these minerals was chiefly helium. There is very little helium in the atmosphere — about 4 volumes in 1,000,000. Small percentages are present in the natural gas of certain localities (especially in Texas), and this is the only practical source of helium. From this source we are able not only to meet our own needs but also to furnish a limited supply to other countries (Figs. 190, 191).

Properties and uses of helium. Next to hydrogen, helium is the lightest of all elements. *It is the most difficult of all gases to liquefy.* The Dutch physicist Onnes was the first to liquefy it (1908), and his success was regarded as one of the great achievements of science. Liquid helium boils at – 268.9°; solid helium melts at – 272.2°. The latter approaches *absolute zero* (– 273°), a temperature which is believed to mark the entire absence of molecular motion.

The great importance of helium lies in its use for inflating balloons and dirigibles (Fig. 191). It has 7½ per cent less

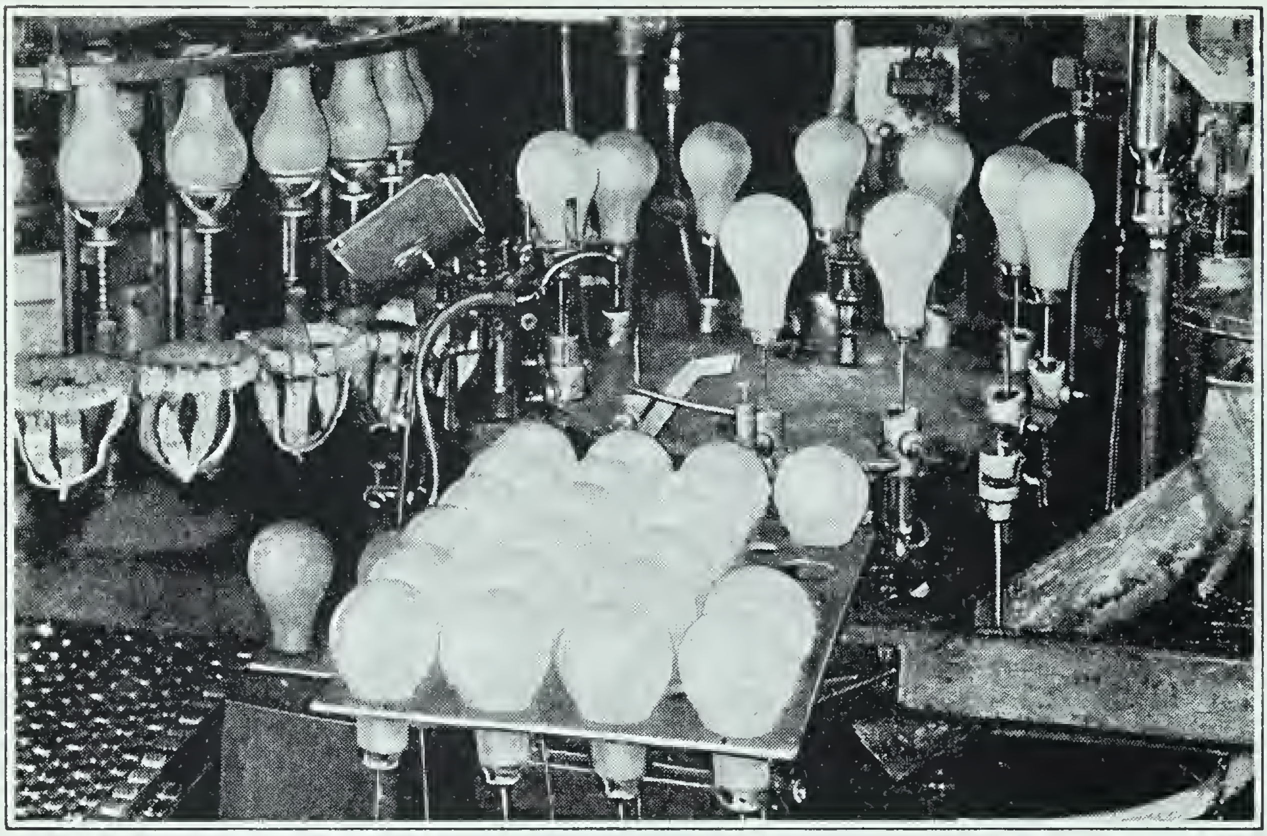


Fig. 192. Filling electric-light bulbs with argon

lifting power than hydrogen; but since it will not burn, it is safer than hydrogen, which is very inflammable.

Neon, argon, krypton, and xenon. With the exception of helium, which we get from natural gas, the remaining members of the group of "lazy" elements are all obtained from liquid air, as will be described in the following chapter. Neon has a very wide use in the red-glowing "neon signs," and many millions of dollars are involved in their production each year. These consist of glass tubes containing a very small amount of neon, by means of which a current of electricity passes through the tube. The reason light is given off has been explained in connection with the sodium lamp (p. 234). Many electric-light bulbs are now filled with argon (Fig. 192), so that this gas also is used in considerable amounts. Argon does not act on the tungsten wire in the lamp, and it prevents the tungsten from vaporizing and so wasting away. Because of their high cost, krypton and xenon have as yet no commercial uses.

The spectroscope. Not only was the discovery of helium made by the use of the spectroscope (Fig. 193) but a number of other elements have been discovered in this way. This instrument, devised by Bunsen (Fig. 189) and Kirchhoff, is of such great value that it is important to know at least the principle upon which its construction and its use depend.

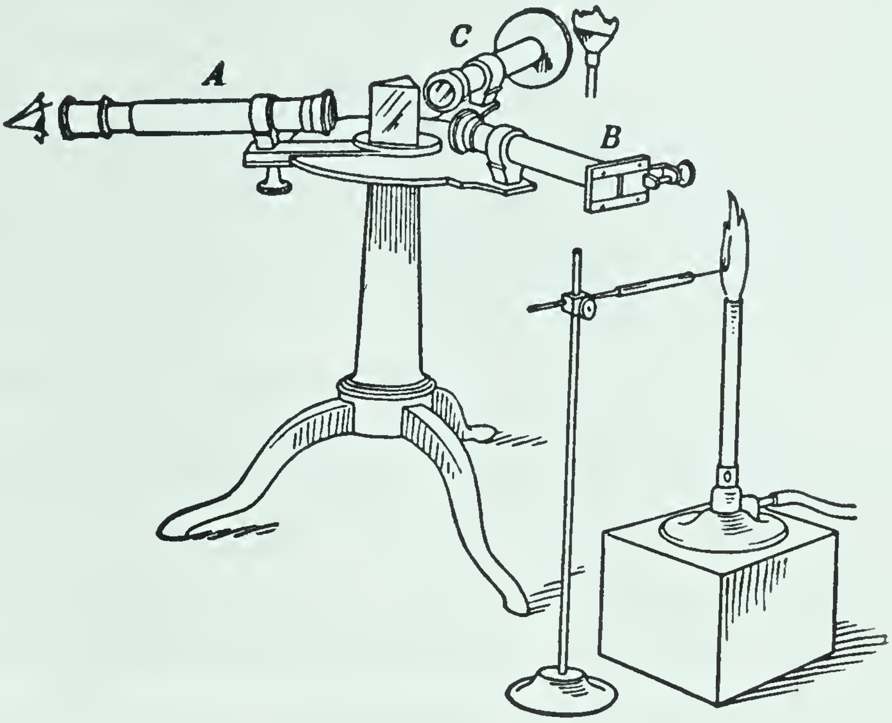


Fig. 193. A simple spectroscope

The substance whose spectrum we wish to examine is placed on a wire and vaporized by the heat of a Bunsen flame. The resulting light waves are separated by the prism and refracted through the tube *A*. The spectrum may be seen by looking into the tube *A*. The tube *C* carries a scale, which is seen along with the spectrum

When a beam of light passes through a triangular prism of glass, it is bent out of its course and comes out at a decided angle with its original direction, as is shown in Fig. 194. Ordinary light is made up of waves of many different wave lengths, and each one is bent, or *refracted*, to a different degree, so that the various colors of which the light is composed are spread out in a band of colors called a *spectrum*. The red waves are the least refracted, the violet the most so. A beam of *white* light gives a continuous band of colors called a contin-

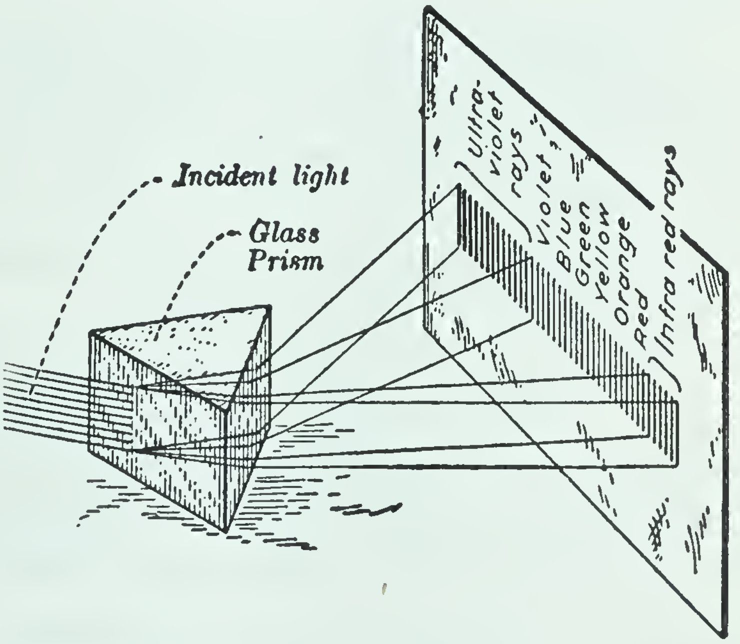


Fig. 194. Diagram showing how a beam of white light is separated into its constituents

uous spectrum (see illustration facing page 270), ranging from red through orange, yellow, green, blue, to violet. The spectrum of any *colored* light is not continuous, but shows merely lines of those colors of which the light is composed.

Now the light given out by the glowing vapor of any element gives a definite spectrum of colored lines, and no two elements have the same spectrum. If we have mapped the spectra of all the elements known to us, then by examining the spectrum of any glowing vapor we can find out just what elements are present in it. A new spectrum would then mean that a new element must be present. In this way helium and a number of other elements were discovered.

Fig. 193 shows how the prism is mounted, and includes the other parts that go to make up a simple spectroscope. Fig. 194 shows simply the prism and the way the beam of light is separated into its constituents.

CHAPTER SUMMARY IN QUESTION FORM

1. Who discovered nitrogen, and when?

2. Where does nitrogen occur (*a*) in the free state? (*b*) in the combined state?

3. Give three physical properties that nitrogen has in common with hydrogen and oxygen.

4. Suppose you were given three bottles filled with hydrogen, oxygen, and nitrogen respectively. How could you identify each?

5. What property of oxygen makes it possible to remove the oxygen from a mixture of oxygen and nitrogen?

6. Explain what happens when a current of air is passed over hot copper.

7. Name three elements with which nitrogen will combine directly under suitable conditions.

8. Give two important uses of nitrogen in industry.

9. (*a*) What plants have the power of taking nitrogen from the air and converting it into compounds of nitrogen? (*b*) What is this process called? (*c*) By what agencies is it brought about? (*d*) Of what value is this process to all of us?

10. (*a*) Name the "lazy" elements. (*b*) Name the discoverer of each. (*c*) Which ones have uses in industry, and for what purposes?

11. What property of the "lazy" elements distinguishes them from all other elements?

12. (*a*) What is meant by the term *absolute zero*? (*b*) How near to absolute zero does the melting point of helium approach?

13. A beam of white light is passed through a triangular glass prism; also a beam of colored light. State the result in each case.

14. (*a*) What instrument is used for obtaining the spectrum of an element? (*b*) How has it enabled chemists to discover new elements? (*c*) Name one element discovered in this way.

THOUGHT QUESTIONS

1. In preparing nitrogen from the air, why not use carbon or a lighted candle for removing the oxygen rather than phosphorus or copper?

2. From the structure of its atom, should you expect nitrogen to combine readily with oxygen?

3. Give two reasons why the "lazy" elements remained so long undiscovered.

4. Why do the "lazy" elements form no compounds?

5. (*a*) What is the great objection to the use of hydrogen for inflating airships? (*b*) Why not use nitrogen for the purpose?

6. Mention different ways in which a farmer enriches the soil.

7. (*a*) Why not use nitrogen as a fire-extinguisher in place of carbon dioxide? (*b*) Why not use it in the manufacture of soda water in place of carbon dioxide?

8. Which of the following statements are true and which false? (*a*) Pure nitrogen is prepared by passing air over hot copper. (*b*) Nitrogen is more difficult to liquefy than helium. (*c*) Nitrogen is a poisonous gas, since an animal immersed in it soon dies. (*d*) Some electric lamps are filled with argon. (*e*) Nitrogen is less active than either oxygen or argon. (*f*) The percentage of nitrogen in our bodies is greater than the percentage in the earth's crust. (*g*) The nitrogen in the tissues of our bodies comes from the air we inhale.

OPTIONAL EXERCISES

1. (*a*) Make a list of names of the elements so far studied. (*b*) Find in the dictionary the derivation of each name. (*c*) Do you think the name of each has been appropriately chosen?

2. A student prepared nitrogen by heating 10 g of ammonium nitrite. (*a*) Calculate the weight of the nitrogen set free. (*b*) Calculate its volume.

CHAPTER XXIV

The Atmosphere

[The Largest Ocean in the World]

At the bottom of the ocean. We all know something about the oceans of water that cover a large part of the earth's surface, sometimes reaching a depth of six or seven miles. But few of us stop to realize that the entire earth is covered with a much deeper ocean of gases, which we call the *atmosphere.* The mixture of gases which composes the atmosphere extends many miles in height — certainly more than one hundred miles. It is densest at the earth's surface, and gradually thins out as the distance from the earth increases. We live at the bottom of this ocean.

Some results of living at the bottom of the atmosphere. Our bodies have been developed to feel comfortable and work well at the bottom of the atmospheric ocean, which presses upon them with a weight of about fifteen pounds on each square inch of surface. Our lungs are suited to act at about this pressure. High-mountain climbers, and aviators who go up more than four or five miles, suffer both from lack of oxygen in the thin air and from the lower pressure, and they carry with them compressed oxygen to correct both troubles for their lungs. Divers who work on bridge foundations or about sunken ships must have oxygen to breathe, but must have it under pressure according to depth; for every thirty-three feet of water equals the pressure of the whole atmosphere.

The make-up of the air. By *air* we mean the portion of the atmosphere that is in any place in which we happen to be. The gases that make up the air collected in open fields, and their approximate volumes, are as follows:

Oxygen	21 volumes in 100 volumes of dry air
Nitrogen	78 volumes in 100 volumes of dry air
Water vapor	Variable within wide limits
Argon	94 volumes in 10,000 volumes of dry air
Carbon dioxide	3 to 4 volumes in 10,000 volumes of dry air
Hydrogen, helium, neon, krypton, xenon, ozone . .	Traces

In addition the air always carries particles of dust, bacteria, and forms of plant life, such as yeast cells. The air of thickly populated districts contains smoke particles, and often various gases resulting from manufacturing plants and automobiles.

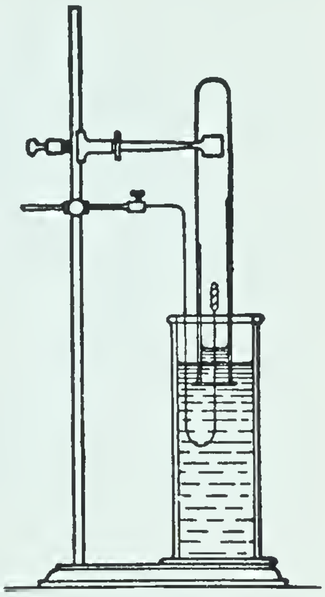


FIG. 195. The analysis of air

Phosphorus (placed on the end of the wire) removes the oxygen from air and leaves the nitrogen

Water vapor in the air. The quantity of water vapor that may be present in the air varies with the temperature. This is shown in the following table, which gives the weight in grams of the water vapor that 1 cubic meter of air can absorb at the temperature indicated:

Temperature	0°	10°	20°	30°
Weight of water	4.8 g	9.9 g	17.1 g	30 g

When air contains all the moisture it can take up at a given temperature, it is said to be *saturated*. The Weather Bureau reports the percentage of saturation from day to day and calls it the *humidity*.

Constituents of the air that are necessary for life. The constituents of air that we must have are oxygen, nitrogen, water vapor, and carbon dioxide. The oxygen in the atmosphere directly supports life, keeping up the heat of the body by oxidizing foods and worn-out tissues in the body. The nitrogen dilutes the oxygen and so regulates its action. The water vapor prevents too much evaporation of the water present in living things. The carbon dioxide is an essential plant food.

The analysis of air. How can we measure the percentage of each of the constituents present in the air? A number of methods have been devised for doing this, among which are the following:

1. ***Oxygen.*** A measured volume of air (from which carbon dioxide and water vapor have been removed) is brought in contact with phosphorus, which combines with all the oxygen. The loss in the volume of air gives us the volume of oxygen (Figs. 195, 196).

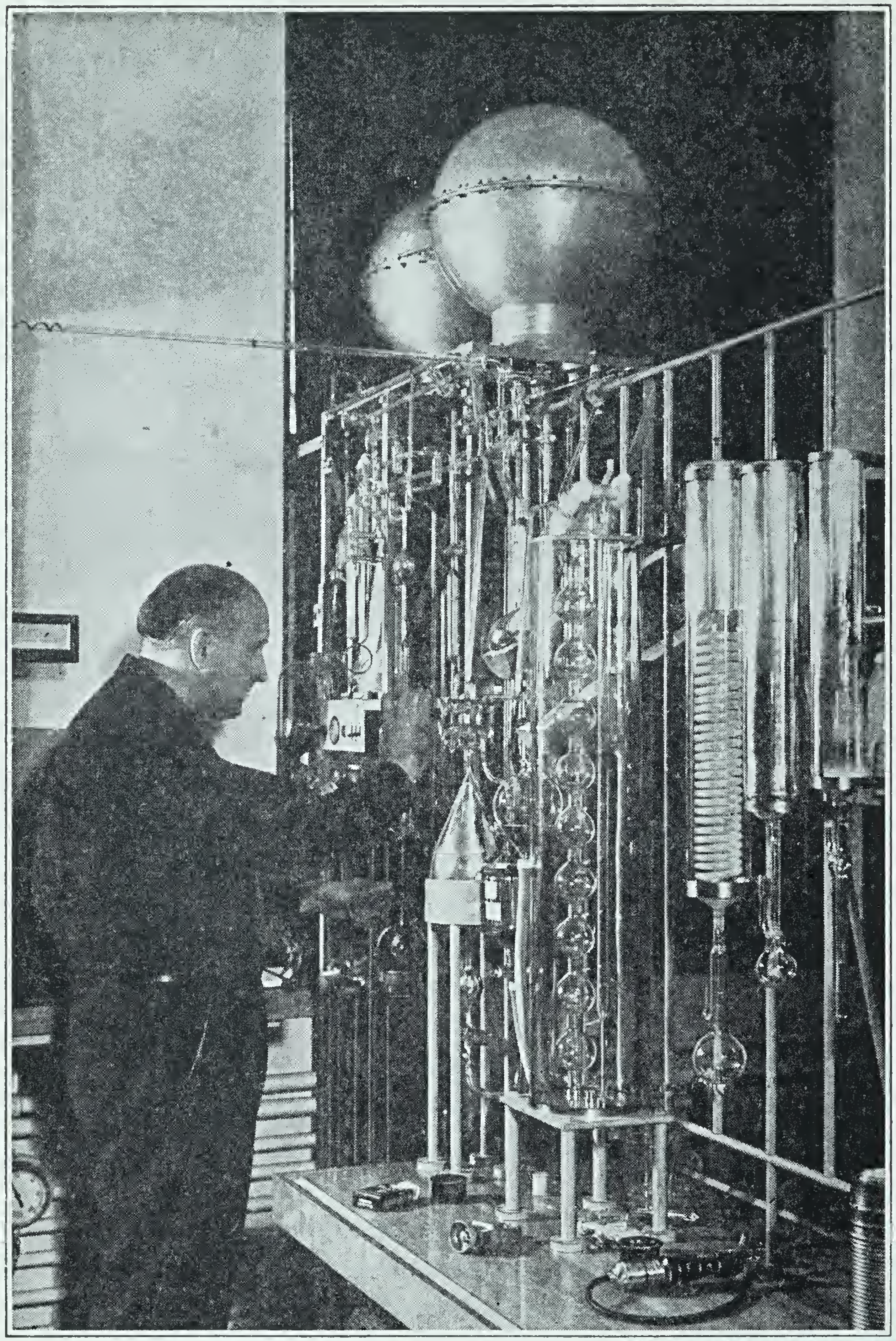


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FIG. 196. Analyzing samples of air collected about thirteen miles above the earth's surface by Captain Stevens and Captain Anderson in their stratosphere flight (1935)

It was found that the samples had about the same relative composition as pure air collected at the earth's surface. (Reproduced from the *National Geographic Magazine* with special permission)

2. ***Nitrogen.*** The gas remaining after the removal of the oxygen is passed over hot magnesium, which combines with the nitrogen:

$$3\,Mg + N_2 \longrightarrow Mg_3N_2$$

This second loss in volume equals the volume of nitrogen removed. The small volume of gas remaining is made up of argon and of the other rare elements that are present in the air.

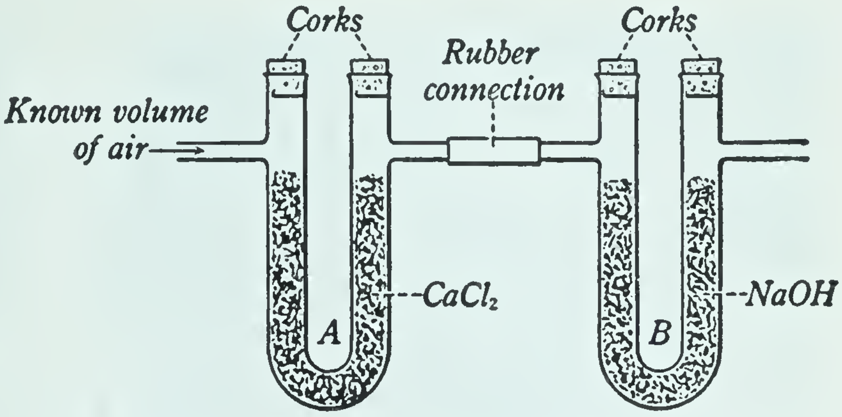


Fig. 197. Apparatus used in determining the percentage of carbon dioxide and water vapor in air

3. ***Water vapor and carbon dioxide.*** These two can be measured by passing a known volume of air through two tubes, the first filled with calcium chloride, and the second with sodium hydroxide (Fig. 197). The calcium chloride removes the water vapor, and the sodium hydroxide removes the carbon dioxide. The tubes and contents are weighed separately before and after the air is passed through them. The increase in their weights gives us the *weights* of water vapor and of carbon dioxide in the original volume of air.

Some processes tend to increase the carbon dioxide in air. Not only do large quantities of carbon dioxide escape into the atmosphere from volcanoes, crevices in the earth's crust, and manufacturing operations, but certain more widespread processes give off this gas. Chief among these processes are the following:

1. ***Respiration.*** In the respiration of animals some of the oxygen in the inhaled air is absorbed by the blood and carried to all parts of the body. There it combines with the carbon of worn-out tissues and with that of fuel material supplied by digestion. The products of oxidation are carried back to the lungs, and exhaled largely in the form of carbon dioxide and water vapor.

2. ***Combustion.*** All the ordinary fuels contain large percentages of carbon. When the fuel is burned, the carbon is oxidized to carbon dioxide. It has been estimated that the

burning of the fuels mined during the past fifty years has poured into the atmosphere 180 billion tons of carbon dioxide.

3. *Decay of organic matter.* When organic matter decays in the air, much of its carbon is oxidized to carbon dioxide.

Certain processes tending to diminish the carbon dioxide in the air. There are three general processes that diminish the quantity of carbon dioxide in the atmosphere:

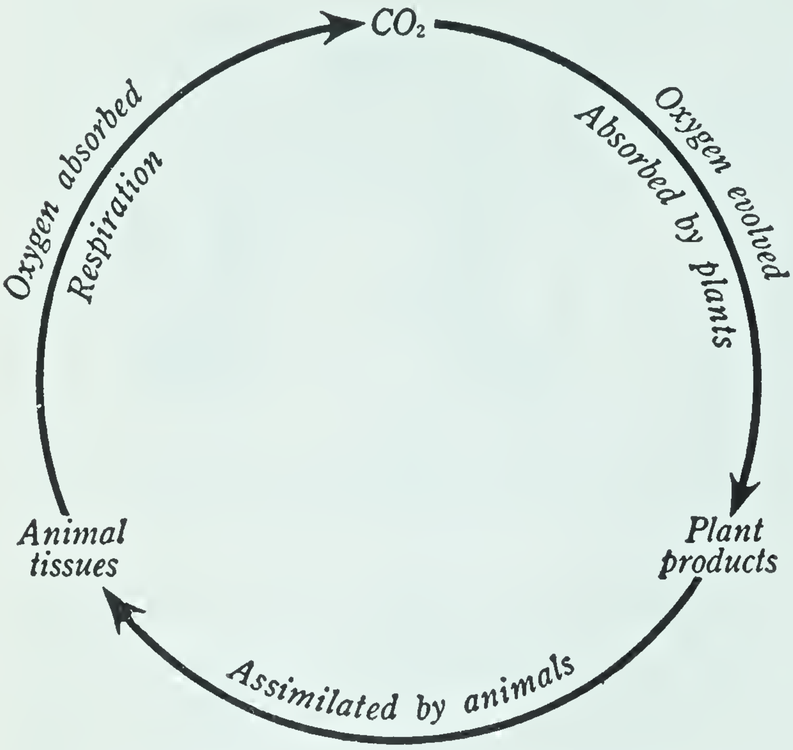


Fig. 198. The cycle of carbon dioxide in nature

1. *The growth of plants.* When growing in sunlight, green plants take up carbon dioxide from the air, building the carbon into their growing parts and returning a part of the oxygen to the air. It is from this source that plants obtain their entire supply of carbon.

2. *The weathering of rocks.* Large quantities of carbon dioxide are constantly being taken out of the atmosphere because of its combination with various rock materials.

3. *Solution in ocean waters.* The water of the oceans dissolves vast quantities of carbon dioxide from the air. Some of this is built into the shells of sea animals as calcium carbonate ($CaCO_3$).

The cycle of carbon dioxide in nature. From what we have learned it is evident that the carbon dioxide taken from the air by plants is later returned to it. Plants take up the carbon dioxide and build it into various plant products, many of which are used as food. Animals feeding on these products assimilate them, and later, through respiration, return much of the carbon in them to the air in the form of carbon dioxide; and in this manner the cycle is completed and constantly repeats itself (Fig. 198).

Composition of the air nearly constant. While each process just described tends to alter the composition of the air, yet the results of a great many analyses of dry air collected from year to year in the open fields show that the percentages of oxygen, of nitrogen, and of carbon dioxide are very nearly constant. How do we account for this?

The answer is this: (1) The changes caused by combustion, respiration, and decay on the one hand, and by the growth of green plants, the weathering of rocks, and solution in sea water on the other, tend to balance each other. (2) The volume of the air is so vast, and the changes that occur are so small in comparison with its total volume, that variations are difficult to detect, especially since the winds keep the air in motion and so prevent marked local changes. If there should be any processes at work that lock up oxygen or carbon dioxide *permanently*, then all life would eventually end.

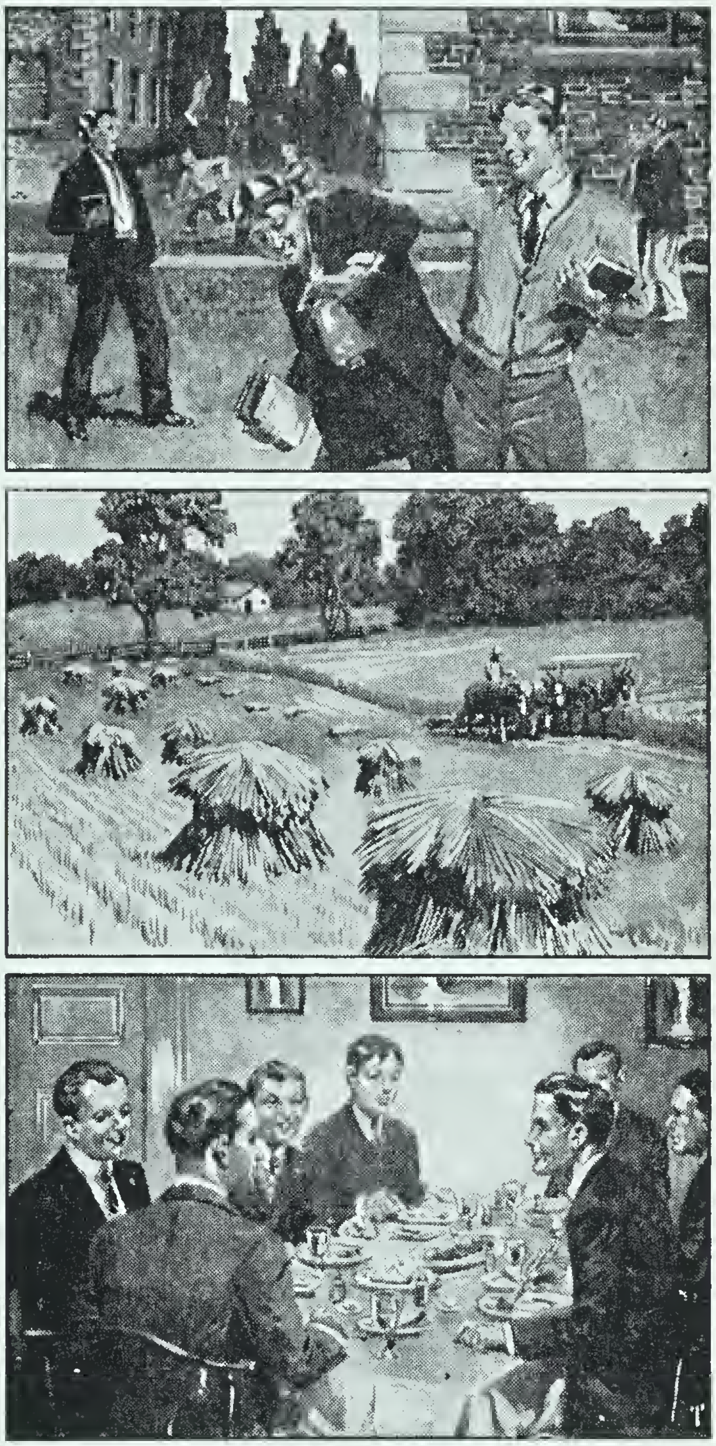


FIG. 199. An illustration of the cycle of carbon dioxide in nature

Do these pictures suggest to you any changes representing the cycle of carbon dioxide in nature? If so, explain

Are the oxygen and nitrogen in the air combined or simply mixed together? That these two gases are simply mixed together in the air may be proved in a number of ways, among which are the following:

1. While the percentages of oxygen and nitrogen are nearly constant, they are not so constant as they would be were the two elements combined in the form of a compound.

2. When liquid air boils, the nitrogen passes off first. Were the nitrogen and oxygen combined, they would pass off together, just as the hydrogen and oxygen in water do when water is boiled.

Impure air. The approximate difference in the percentages of oxygen, carbon dioxide, and moisture present in inhaled and exhaled air is shown in the following table:

CONSTITUENT	INHALED AIR	EXHALED AIR
Oxygen	21.00%	16.00%
Carbon dioxide	0.04%	4.38%
Water vapor	Variable	Saturated

The unpleasant or even injurious effects that come from the impure air of crowded rooms seem to be due neither to lack of oxygen nor to too much carbon dioxide. They can be traced to several causes. (1) In a crowded room or public hall the temperature rises much above that of comfort (68°–70° F.). (2) At the same time the air becomes more nearly saturated with moisture from the breath and perspiration of those present. The humidity for comfort is about 50 per cent. Very humid air is depressing, for it interferes with normal evaporation from the lungs and skin. Fans do not lower the temperature of a room, but by stirring up the air they help evaporation by bringing unsaturated air in contact with the skin. (3) Dust particles are an irritation to nose and throat, and they are more numerous in a room full of people. (4) Disease germs of various kinds are on these particles and on moisture droplets from people who sneeze and cough; as a result many "colds" result from crowded rooms.

All these causes together result in discomfort, sleepiness, headache, and even infections.

Ventilation. It should be the aim of proper ventilation to correct these ills. Fresh air from the outside, admitted by door or window, is of course the simplest way to get ventila-

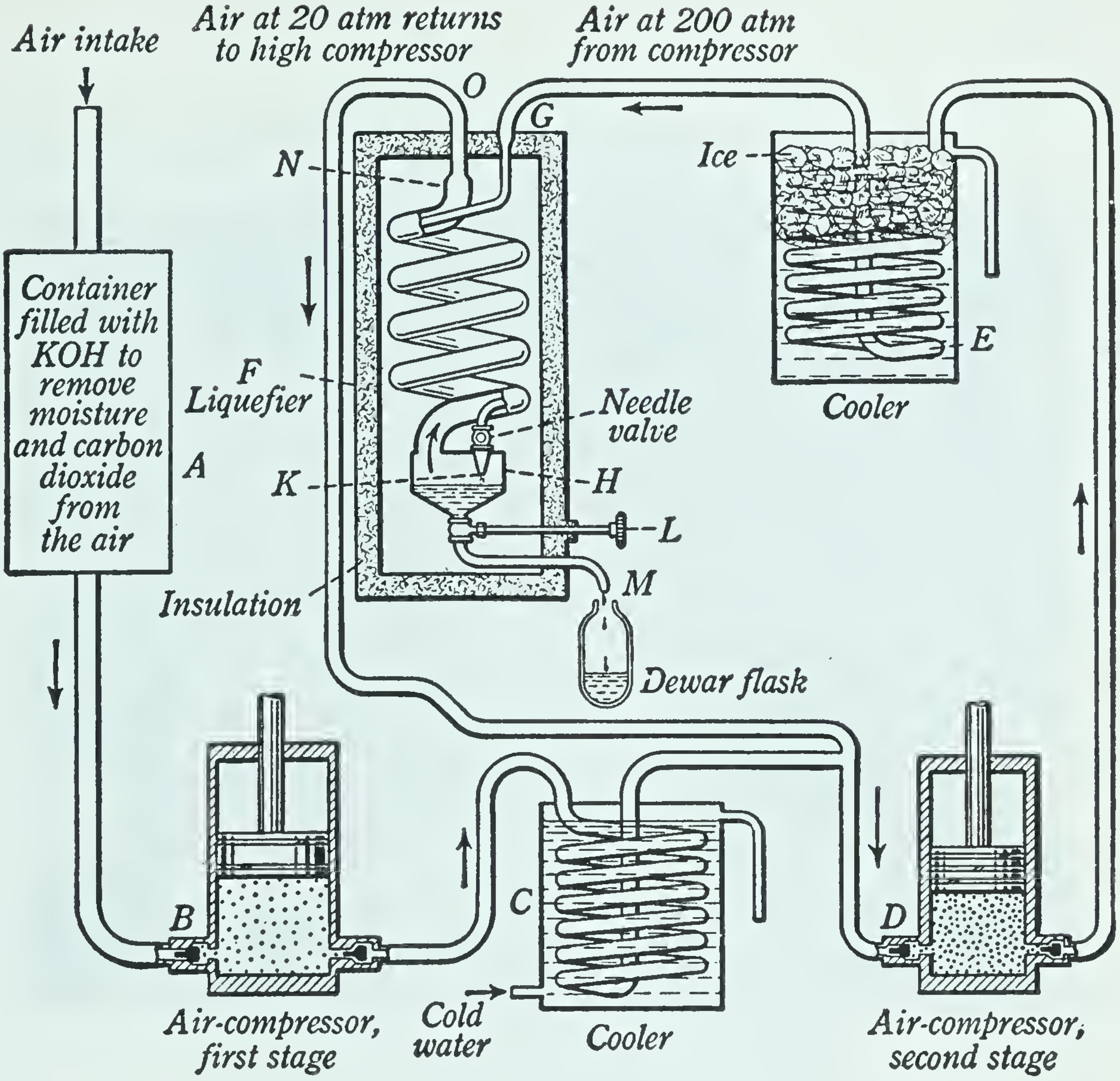

Air intake
Air at 20 atm returns to high compressor
Air at 200 atm from compressor
O
G
N
Ice
Container filled with KOH to remove moisture and carbon dioxide from the air
A
F Liquefier
Needle valve
K
H
L
M
E
Cooler
Insulation
Dewar flask
B
C
D
Air-compressor, first stage
Cold water
Cooler
Air-compressor, second stage

Fig. 200. The steps in the liquefaction of air

The air enters the apparatus at the air intake and passes through a chamber *A* filled with absorbents for moisture and carbon dioxide. It then enters the air-compressor *B*, where it is highly compressed. Heat is evolved in this process, and the compressed hot air is cooled by cold water in the cooler *C*. It undergoes further compression in *D* and is again cooled in *E*. The highly compressed cold air then enters the liquefier *F*. Inside the liquefier the copper tube *G* is enclosed in a tube *N* of larger diameter, and the two concentric tubes form a spiral. At *K* there is a very small opening controlled by a needle valve. Through this hole some of the compressed air escapes into the cup *H* and expands to a lower pressure. In expanding, the air becomes very cold, and is led back through the outer tube *N* to cool the incoming air within the inner tube *G*. As the process continues, the air in tube *G* becomes increasingly cold until it reaches the temperature of liquefaction, when drops of liquid air form and collect in the cup *H*. By means of the valve *L*, the liquid air is drawn off into the Dewar flask through *M*. The cold expanded air returns to the compressor *D* through the pipe *O*

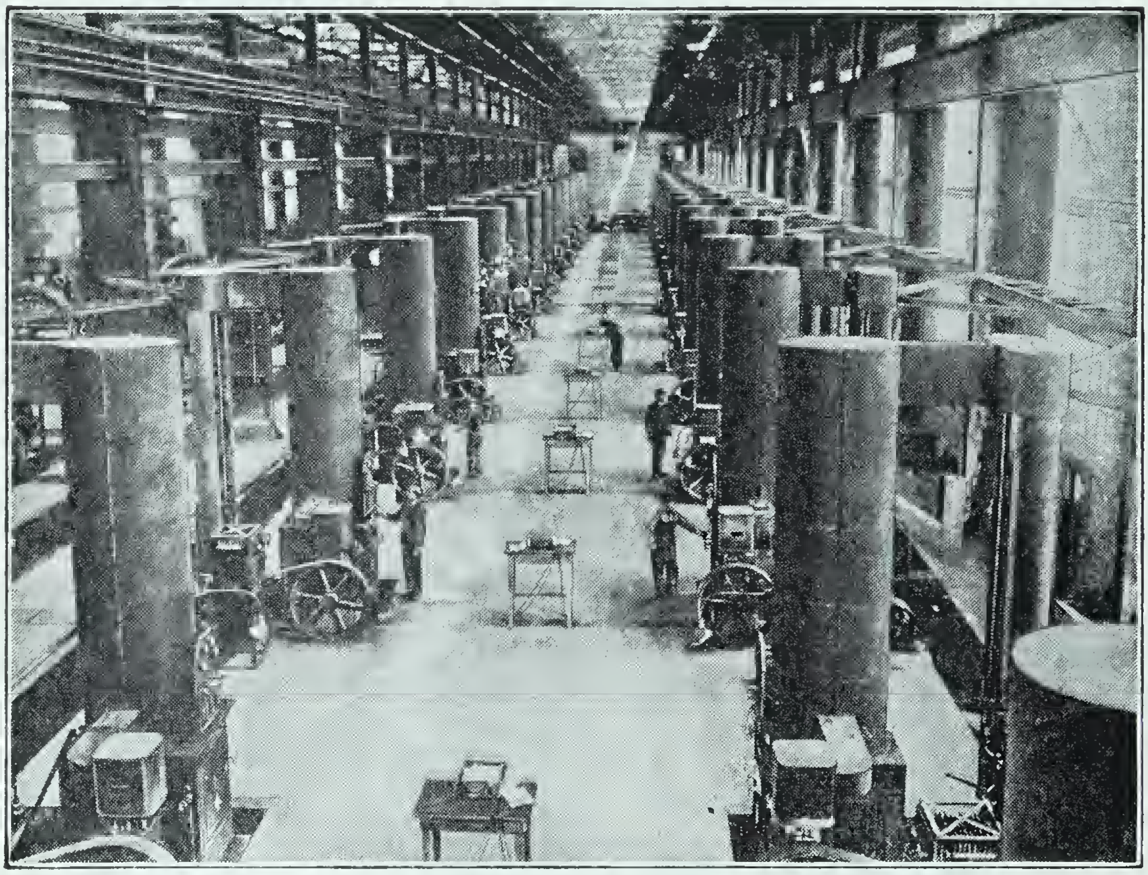


Fig. 201. A liquid-air plant in operation

Whereas Fig. 200 shows the different steps required in liquefying air, this illustration gives a view of a liquid-air plant in actual operation. The plant shown is one built during the World War at Muscle Shoals, Alabama. The engine used in compressing the air appears on the extreme left. The compressed air is first cooled by water and then still further cooled by being made to run small engines, one of which is shown at the base of each of the large columns. In this process, energy of heat is changed into energy of motion, which results in the cooling of the compressed air to a temperature at which it liquefies as it passes through the liquefier (see Fig. 200). In the Muscle Shoals plant the liquid air is used for the preparation of nitrogen. To separate the nitrogen from the oxygen, the liquid air is forced into the top of the large columns shown in the figure. As it flows down the metal plates on the inside of the columns the nitrogen present separates (boils) in gaseous form, since it boils more readily than the oxygen. This process serves for the commercial preparation of both nitrogen and oxygen. In the Muscle Shoals plant three hundred tons of nitrogen can be obtained each twenty-four hours

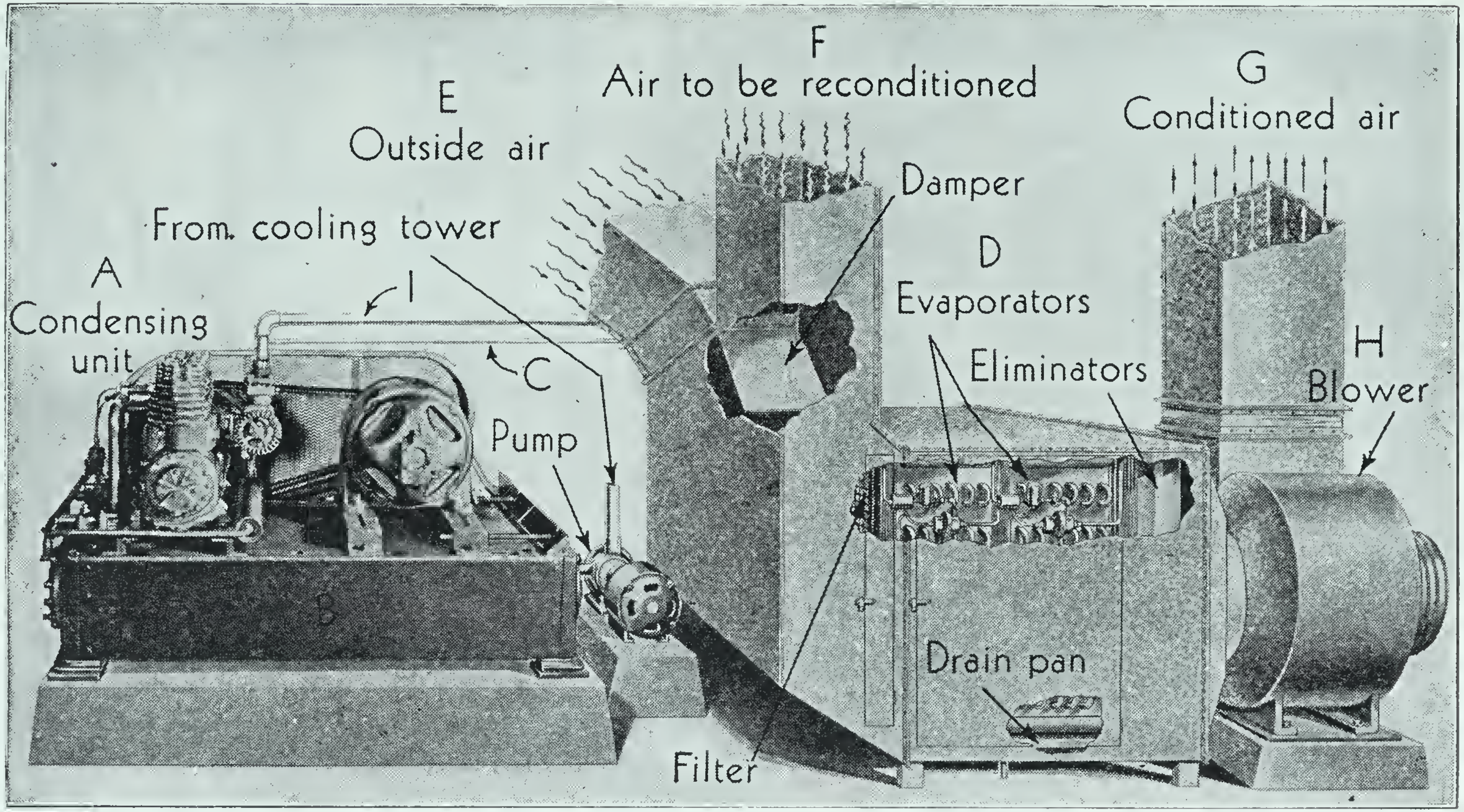

F
Air to be reconditioned
E
Outside air
G
Conditioned air
Damper
From cooling tower
D
Evaporators
A
Condensing unit
I
C
Eliminators
H
Blower
Pump
B
Drain pan
Filter

FIG. 202. A form of air-conditioning apparatus. It operates on the same principle as the mechanical household refrigerator

A set of tubes is filled with an easily condensed gas. This gas is liquefied by pressure in the condensing unit *A*. The heat set free is absorbed by a current of water. The resulting liquid runs into the evaporators *D*, where it vaporizes with absorption of heat that keeps the pipes cold. The incoming air passes over these pipes. The air is thereby cooled, and any excess moisture present in it condenses and collects in the drain pan. The cool, dry air is then forced by the blower *H* through the building. (Courtesy of General Motors Corporation)

tion, but its value depends a good deal on the state of the fresh air admitted and on preventing harmful drafts.

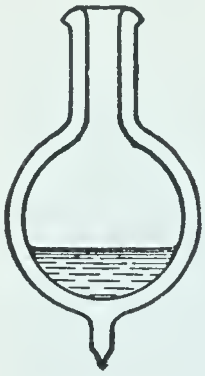


Fig. 203. Liquid air in a Dewar flask

The ideal air condition varies with the occupation, clothes worn, and other factors. An expert who has made an extensive study of ventilation states that "for the home and office, and for any other situation in which the occupation and other conditions are comparable with those of the school, the standards of the New York State Ventilation Commission are probably satisfactory, namely, not over 68° F., without artificial humidification, and with a moderate supply of fresh air from the open window."

Air conditioning. By *conditioning* the air is meant (1) getting it as clean as possible from dust and germs; (2) keeping it at the right temperature and humidity (Fig. 202).

Using the same air over and over raises the percentage of carbon dioxide, but, within limits, this does not seem to be injurious. Houses, hotels, office buildings, stores, railway cars — in general, all closed spaces where people gather — are now being "air-conditioned."

Liquid air. We have learned that all gases, if cooled and compressed enough, may be changed into liquids or even solids. Some gases, such as sulfur dioxide (the gas formed when sulfur burns in air) (p. 85), are easily liquefied; others, such as oxygen and nitrogen, with more difficulty; while helium is the most difficult of all to liquefy (p. 271).

Air was first obtained in the liquid state about sixty years ago. The method used has been improved (Figs. 200, 201) until now liquid air is an article of commerce. It is essentially a mixture of liquid nitrogen (boiling point, – 195.8°) and liquid oxygen (boiling point, – 183°). The extremely low temperature of liquid air may be judged from the fact that it freezes mercury to a mass so hard that the mercury may be used as a hammer head for driving nails.

The difference in the boiling points of oxygen and nitrogen makes it possible to separate a mixture of these two gases by distillation; in this way oxygen and nitrogen are obtained on a commercial scale (pp. 81, 284). From the same source and by the same method neon and argon are obtained.

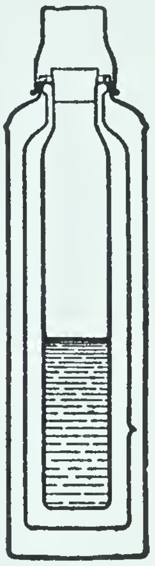


Fig. 204. A thermos bottle

Dewar flasks; thermos bottles. Liquid air may be kept for some hours in a special form of flask devised by the Scottish scientist Dewar, called a *Dewar flask.* This consists of two concentric vessels (Fig. 203) of any suitable shape. These are joined together at the upper rim only, and the space between them is exhausted by an air pump. The vacuum serves as the best possible insulator to prevent conduction of heat. The surface of the outer flask is often silvered in order to reflect heat from outside and prevent its absorption. Thermos bottles (Fig. 204) and receptacles of various shapes are made on the same plan and are very effective for keeping liquids either hot or cold for several hours.

CHAPTER SUMMARY IN QUESTION FORM

1. (*a*) Name five gases present in appreciable percentages in the air. (*b*) Give the volumes of each of these gases present in 100 volumes of dry air.

2. Name five gases mere traces of which are found in the air.

3. (*a*) Name four constituents of the air that are necessary to life. (*b*) What part does each of these play in supporting life?

4. How can you determine the percentage (*a*) of oxygen in the air? (*b*) of nitrogen? (*c*) of carbon dioxide? (*d*) of water vapor?

5. Name (*a*) three processes occurring in nature that tend to increase, and (*b*) three processes that tend to decrease, the quantity of carbon dioxide in the air.

6. Do the results of many analyses of the air collected in the open fields show that the percentages of oxygen, nitrogen, and carbon dioxide (*a*) are constant? (*b*) are very nearly constant? (*c*) vary through a wide range? (*d*) gradually change as the years pass?

7. (*a*) Are the nitrogen and oxygen in the air combined or simply mixed together? (*b*) Give two reasons in support of your answer.

8. Which of the following statements is correct? (*a*) Air is a compound. (*b*) Air is an element. (*c*) Air is a mixture of elements. (*d*) Air is a mixture of compounds. (*e*) Air is a mixture of elements and compounds.

9. Are the injurious effects resulting from poor ventilation due to (*a*) lack of oxygen? (*b*) excess of carbon dioxide? (*c*) high temperature? (*d*) too much moisture?

10. (*a*) What do we mean by "air conditioning"? (*b*) State the principles involved in a common form of apparatus used for air conditioning.

11. (*a*) Name a gas that is easily liquefied. (*b*) Name the one that is the most difficult of all to liquefy.

12. Of what is liquid air essentially composed?

13. (*a*) What is the name of the kind of vessels in which liquid air is kept? (*b*) Why are such vessels better for this purpose than ordinary flasks?

THOUGHT QUESTIONS

1. Why is the atmosphere densest at the earth's surface?

2. Since oxygen, like water, can be obtained in the form of a gas, a liquid, or a solid, why do we say that water is a liquid and that oxygen is a gas?

3. How do you account for the presence of ozone in the atmosphere?

4. When an open vessel containing liquid air is placed on a cake of ice, the liquid air boils violently. Why?

5. Carbon dioxide is much the heaviest of the gases present in the air. Why does it not settle to the ground?

6. Show how it is possible for the carbon in the coal which we burn to return to us as a constituent of bread or of meat.

7. (*a*) Why do windows sometimes "sweat" in wintertime? (*b*) Does the moisture collect on the inside or the outside of the window glass?

8. Suppose you passed 30 liters of dry air through a tube containing hot copper (Fig. 184). (*a*) What volume of nitrogen should you obtain? (*b*) What substances would be left in the tube? (*c*) How much would the contents of the tube increase in weight (the air having been under standard conditions)?

9. Which of the following statements are true and which are false? (*a*) An electric fan running in a room lowers the temperature in the room. (*b*) Persons become drowsy in a crowded room because of the increase in the percentage of carbon dioxide. (*c*) Liquid nitrogen boils at − 195.8°, while liquid oxygen boils at − 183°; hence, if a mixture of the two (liquid air) is allowed to boil, the oxygen will pass off first. (*d*) The barometric reading decreases as we ascend from the earth's surface, because the force of gravity grows less. (*e*) The higher the temperature of air, the greater the weight of water it will absorb.

10. As a result of breathing, (*a*) what constituent of air is increased? (*b*) what constituent of air is decreased? (*c*) what constituent of air is neither increased nor decreased?

OPTIONAL EXERCISES

1. Compare the boiling points of oxygen, nitrogen, and hydrogen (see Appendix E). When water boils, the hydrogen and oxygen pass off together; but when liquid air boils, the nitrogen passes off first. Account for this difference between liquid air and water.

2. Measure approximately, in cubic meters, the size of your classroom. Suppose that the air in the room is saturated with moisture and that the temperature is 20° C. If now the temperature should fall to 10°, what weight of water would separate, assuming that the quantity of air does not change? (See page 277 for data.)

3. An average home using coal as a fuel burns about 12 tons of coal annually. Supposing that 80 per cent of the coal is carbon and that the combustion is perfect, what weight of carbon dioxide will be formed in the combustion of the 12 tons of coal? How many liters of carbon dioxide will be added to the atmosphere?

CHAPTER XXV

Ammonia

[A Simple, but Very Useful, Compound of Nitrogen]

Compounds got by roundabout ways. Some elements, like oxygen and chlorine, form many compounds by direct union with other elements. But nitrogen is a very inactive element, and for the most part we have to get its compounds in indirect ways. We can build them up step by step from a few simple ones; or we can take more complex ones that living matter gives us, such as the proteins of meat and beans, or the casein of milk, and break them down into simpler ones.

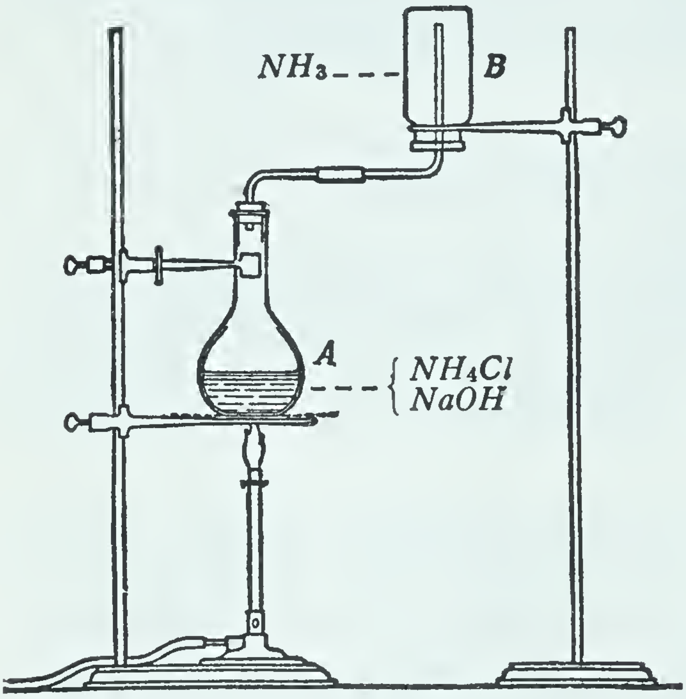


FIG. 205. The preparation of ammonia

Ammonium chloride and sodium hydroxide react when heated together (*A*) and evolve ammonia, which is collected by displacing the air in the bottle *B*. Why is the flask *B* inverted?

In these ways we get a great variety of nitrogen compounds, many of which are unstable. Indeed, as we shall see later on, most high explosives are compounds of nitrogen. Others, more stable, are used as fertilizers, as dyes of many colors, and as medicines. In the present chapter we shall study one of the simplest and most widely used of these compounds, ammonia.

What is ammonia like? Nitrogen and hydrogen unite in different proportions to form several compounds, and of these ammonia (NH_3) is by far the most important. This is a colorless gas with a pungent odor, and is formed when organic matter containing nitrogen decays, being especially noticeable about stables. It is well known to most of us, since its solution in water is sold by all grocers and druggists under the name of *ammonia* or *aqua ammonia*. It is used in our homes as a cleansing agent and as a medicine.

How we get ammonia in the laboratory. In the laboratory we get ammonia from ammonium chloride (NH_4Cl) — a white solid by-product in the manufacture of coal gas — and by other methods as well. *In this compound the group* NH_4 *acts as a univalent radical ion, and is called ammonium.* When ammonium chloride is heated with sodium hydroxide, the ions NH_4^+ and OH^- come together and form the more stable compounds NH_3 and H_2O, as shown in the following equations:

$$NH_4^+, Cl^- + Na^+, OH^- \longrightarrow Na^+, Cl^- + NH_4^+, OH^-$$
$$NH_4^+, OH^- \longrightarrow NH_3\uparrow + H_2O$$

Calcium hydroxide ($Ca(OH)_2$) is often used in place of the more costly sodium hydroxide (Fig. 205).

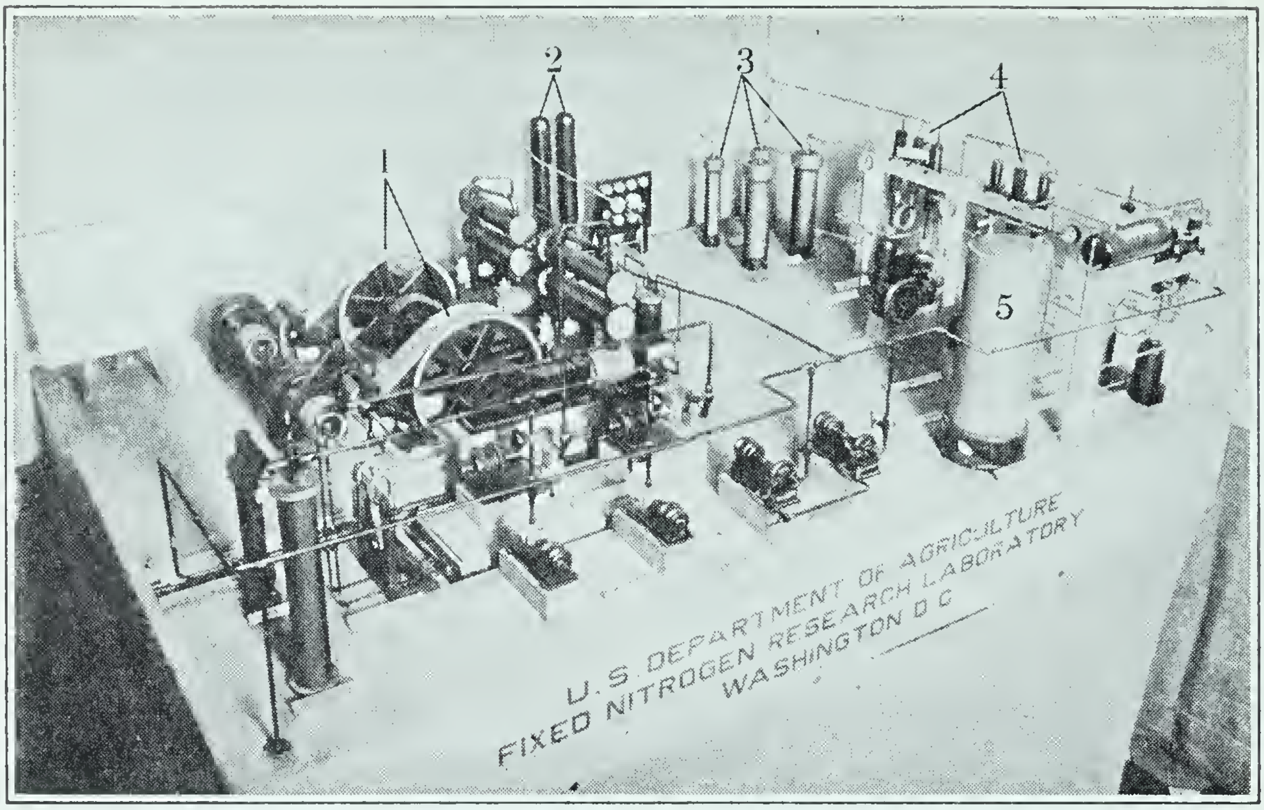
Commercial preparation of ammonia. On a large scale ammonia is prepared by one of the two following methods, each of which requires rather elaborate apparatus.

1. ***By the direct combination of nitrogen and hydrogen — the Haber process.*** When a mixture of nitrogen and hydrogen is heated or subjected to an electrical discharge, a small percentage of ammonia is formed. The small yield is due to the fact that some of the ammonia formed is decomposed again, and there comes a balance, or equilibrium, between the formation of ammonia and its decomposition, which may be expressed as follows:

$$N_2 + 3\ H_2 \rightleftarrows 2\ NH_3$$

The German chemist Haber found that the yield could be greatly increased by putting a very high pressure on the mixture of nitrogen and hydrogen and heating this compressed mixture in contact with a suitable catalyst. This method has been improved by others until now it has become the chief method for obtaining ammonia on a large scale (Fig. 206).

2. ***From coal.*** Ordinary soft coal contains small percentages of nitrogen and hydrogen along with the carbon. When such coal is heated in the absence of air, as is done in the manufacture of coke and coal gas, some of the nitrogen and hydrogen combine to form ammonia. This is separated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U. S. DEPARTMENT OF AGRICULTURE
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Fig. 206. A small model of a plant designed for the preparation of ammonia by the direct union of nitrogen and hydrogen

The nitrogen and hydrogen, mixed in the proportion of 1 volume of nitrogen to 3 of hydrogen, are compressed by engines marked 1. The compressed gases are then forced through the different tubes and cylinders marked 2, 3, and 4, which contain materials for purifying the gases and a suitable catalyst for causing the gases to combine. The resulting ammonia is stored in the container marked 5

from the other compounds formed, and is either dissolved in water, forming the *aqua ammonia* of commerce, or else absorbed in acids, with which it forms salts that are of great value, especially as fertilizers.

Properties of ammonia. Ammonia is a colorless gas and has a strong, suffocating odor. It is just about half as heavy as air. It is easily condensed to a colorless liquid boiling at – 33.3°. This liquid, contained in metal cylinders, is a common article of commerce.

Ammonia is very soluble in water. At the normal pressure of the atmosphere 1 liter of water dissolves 1298 liters of the gas at 0°, and 710 liters at 20°. In dissolving such large volumes of the gas the water expands, so that the density of the solution is less than that of water. The most concentrated commercial solutions have a density of about 0.88 and contain approximately 35 per cent by weight of the gas.

Some chemical changes of ammonia. Ammonia will not support combustion, nor will it burn under ordinary condi-

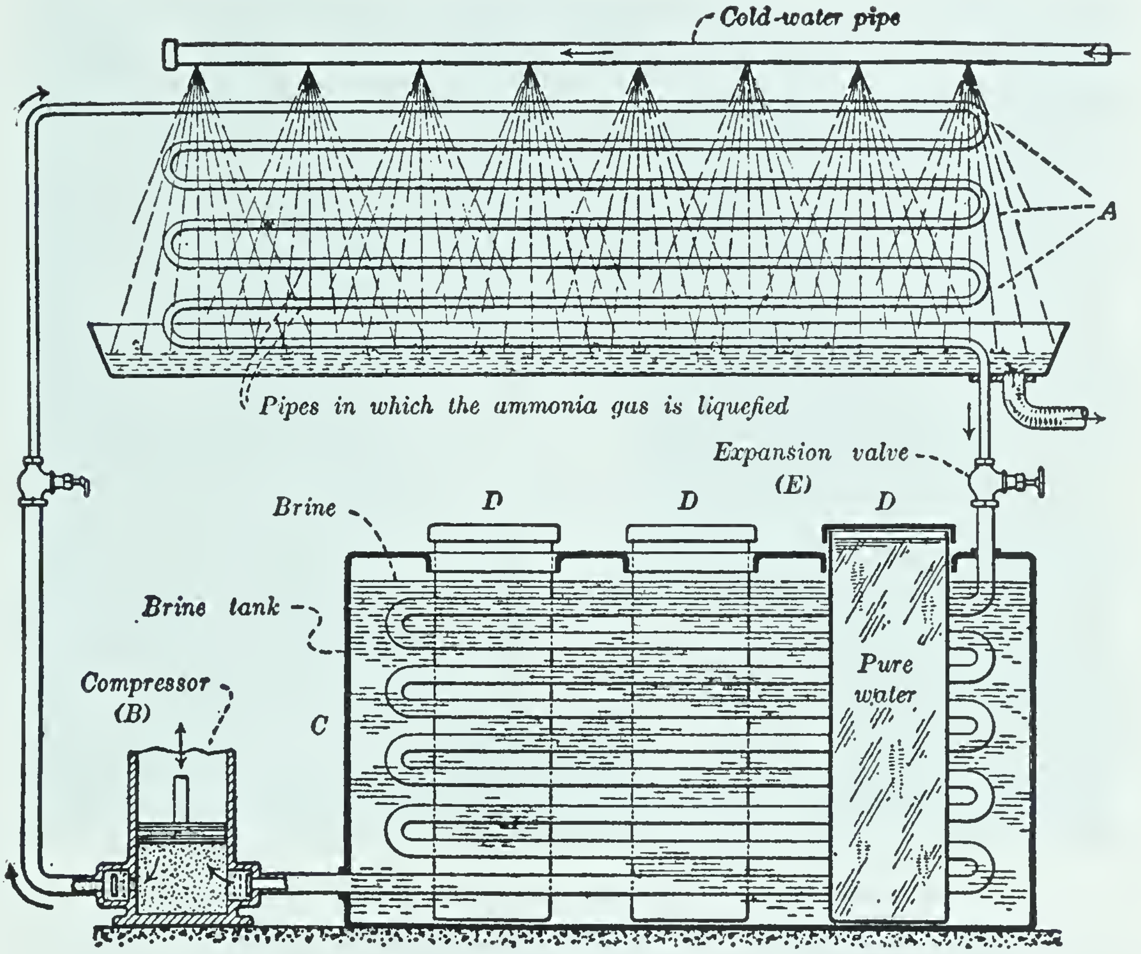


FIG. 207. Illustrating the principle of the ammonia ice machine

Ammonia is compressed by means of a compressor pump *B* and led into the pipes *A*. A great deal of heat is liberated in this process, just as heat is liberated when air is pumped into a tire. This heat is absorbed by sprays of cold water flowing over the pipes as shown in the drawing. Through the combined effect of the pressure and cold, the ammonia is liquefied. The pipes in which the ammonia is liquefied lead into coils in a large tank *C*, nearly filled with a brine which is prepared by dissolving calcium chloride in water. Such a brine may be cooled quite a little below zero without freezing. By means of an expansion valve *E* the pressure upon the liquid ammonia is diminished as it enters the coils. As a result of this decrease in pressure, the liquid ammonia rapidly passes again into the gaseous state, a large amount of heat being absorbed in the process (p. 59). The heat so absorbed is taken from the brine in *C*, with the result that the temperature of the brine is lowered below 0°. Metal vessels *D*, *D*, *D*, filled with pure water, are lowered into the cold brine and left until the water in them is frozen into cakes of ice. The gaseous ammonia is led back to the compressor pump and again liquefied

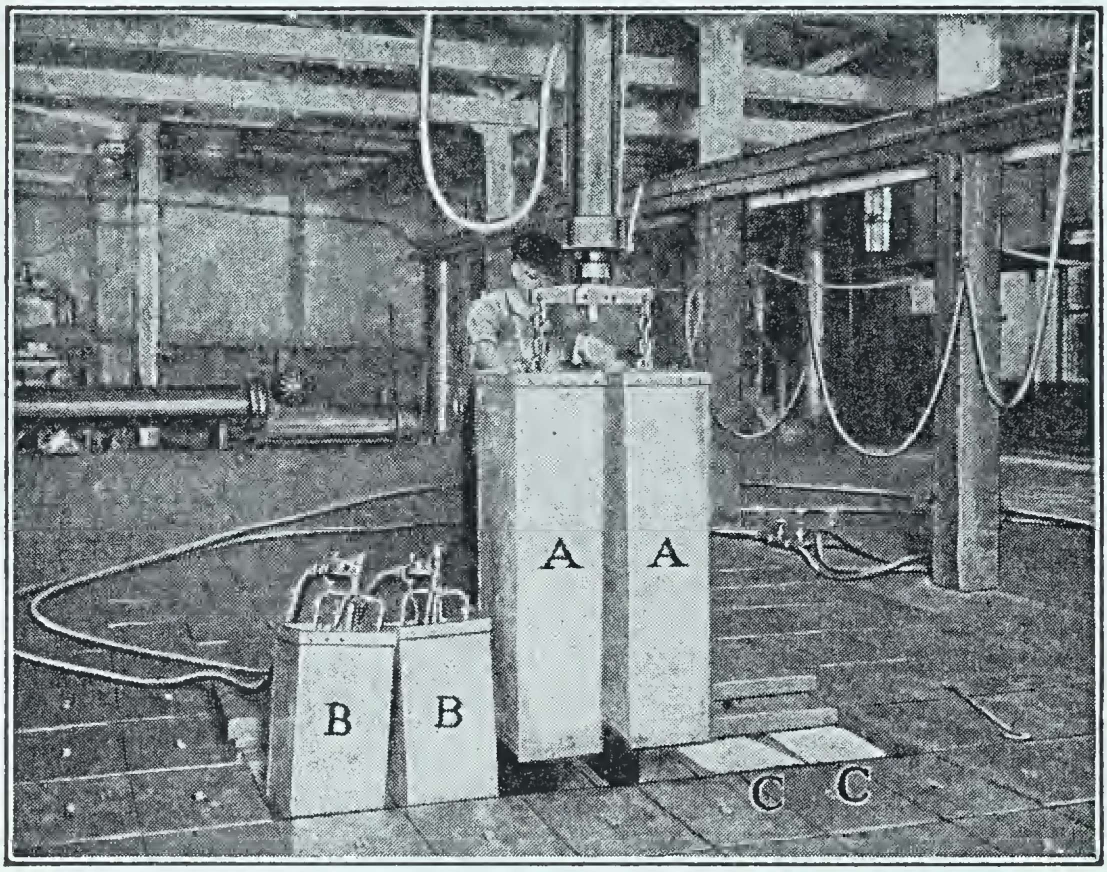
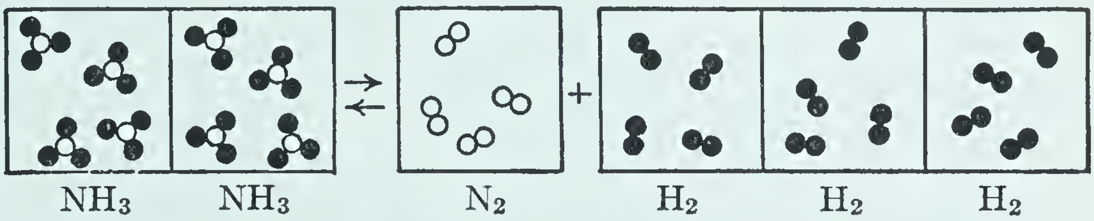


Fig. 208. View of the interior of an ice plant

Fig. 207 illustrates the principle of the ammonia ice machine; Fig. 208 gives a view of the ice plant in actual operation. The floor is made up of small wooden plates, each one forming the cover of one of the metal vessels in which the water is frozen. These vessels are immersed to their rims in the brine tank under the floor. The picture shows two of these vessels, *A*, *A*, being withdrawn from the brine. The water in these is frozen, and the cakes of ice in them are removed by immersing them in warm water for a short time and then inverting them. The vessels are then filled with distilled water, again immersed in the brine, and left until the water is frozen. The picture also shows two vessels, *B*, *B*, from which the ice has just been removed, being filled with water. As the water flows in through the hose at the top, the vessels gradually sink into the brine. The tops of two other vessels, *C*, *C*, are also shown. The water in these is frozen, and the ice is ready to be withdrawn. Refrigerating and cold-storage plants are operated on the same principle as the ice plants, except that the pipes containing the cold compressed ammonia are located in coils about the walls of the rooms; as the pressure is relieved, the heat absorbed reduces the temperature of the room to the desired point tions. In an atmosphere of oxygen it burns with a feeble yellowish flame. When quite dry it is not a very active compound, but when moist it reacts with many other compounds, especially with acids. It is used in making the ammonium salts of commerce and in the manufacture of nitric acid (p. 297), of ice (Figs. 207, 208), and of nylon.



2 vols. of NH_3 $\rightleftarrows$ 1 vol. of N_2 + 3 vols. of H_2

FIG. 209. Since this is a reversible reaction, it may be read in either direction

Composition of ammonia. It is possible to decompose a given volume of ammonia and to measure the volumes of nitrogen and of hydrogen that result. In this way we find that 2 volumes of ammonia yield 1 volume of nitrogen and 3 volumes of hydrogen. These facts are illustrated in Fig. 209, in which the atoms of hydrogen are represented by black circles, and those of nitrogen by white ones.

Ammonium hydroxide (NH_4OH). Neither perfectly pure liquid ammonia nor water has basic properties. Yet when ammonia is dissolved in water the solution has strong basic properties, turning red litmus blue and neutralizing acids to form salts. So it is certain that ammonia and water react with each other to form the ions of a base. Experiments have proved that this base has the composition NH_4OH.

$$NH_3 + H_2O \longrightarrow \overline{NH_4^+, OH^-} \rightleftarrows NH_4^+, OH^-$$

This compound, NH_4OH, is called *ammonium hydroxide,* just as NaOH is called sodium hydroxide. It will be noticed that the ammonium ion NH_4^+ plays the part of a univalent metal ion, since its hydroxide is a base.

Ammonium hydroxide cannot be obtained in a pure state, because it is unstable when concentrated, decomposing into the water and ammonia from which it is formed:

$$\overline{NH_4^+, OH^-} \longrightarrow NH_3 + H_2O$$

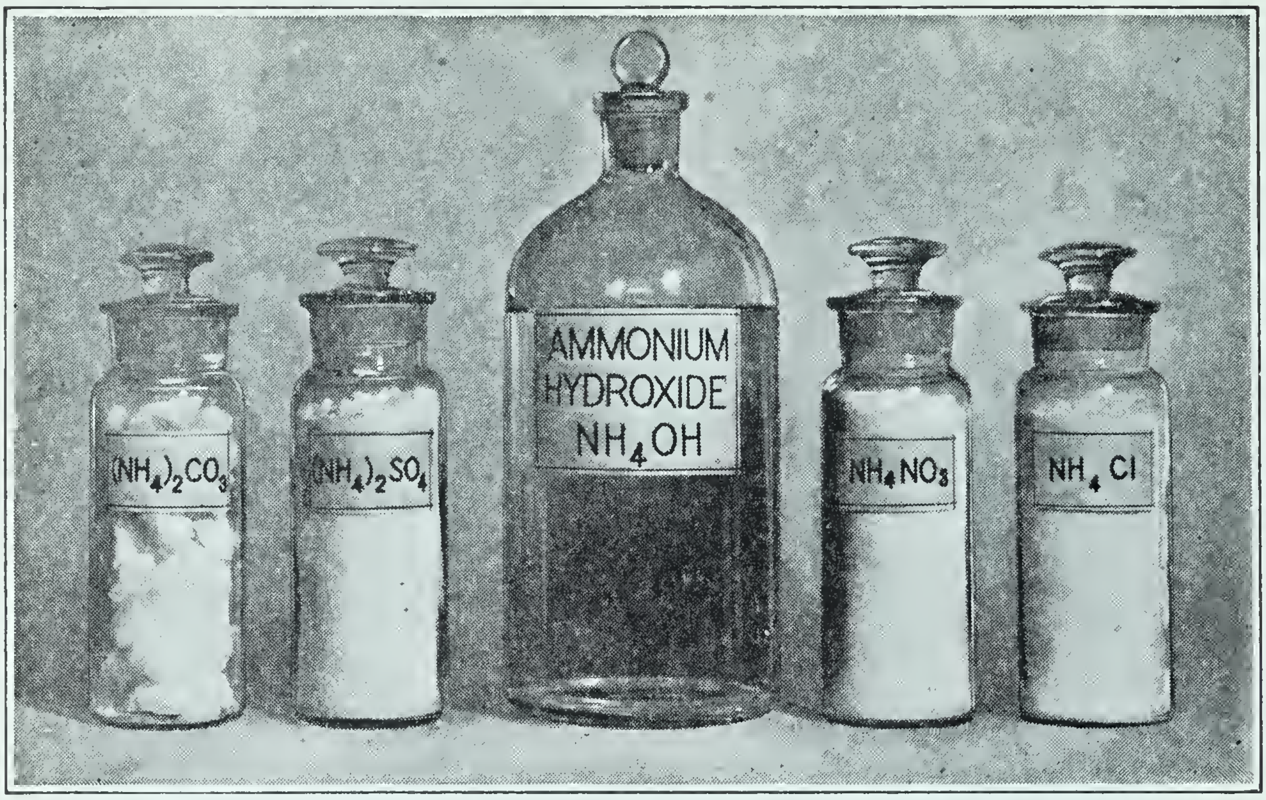


FIG. 210. Some common ammonium compounds. Give the chemical name of each, and classify each as an acid, salt, or base

The solution of ammonia in water is a state of balance, or equilibrium, between ammonia and water on the one hand and the ions of ammonium hydroxide on the other, as expressed in the following equation:

$$NH_3 + H_2O \rightleftarrows NH_4^+, OH^-$$

Ammonium salts. We have seen that ammonium hydroxide acts as a base; and as a base it neutralizes acids, forming salts that are called *ammonium* salts (Fig. 210). With hydrochloric acid it reacts just as does sodium hydroxide, as shown in the two equations

$$NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$$
$$NaOH + HCl \longrightarrow NaCl + H_2O$$

Ammonium salts are nearly all white solids, the most important of which are as follows:

Ammonium chloride (sal ammoniac) (NH_4Cl). This is the most familiar salt. When heated, ammonium chloride partly decomposes into ammonia and hydrogen chloride, which recombine as the temperature falls:

$$NH_4Cl \rightleftarrows NH_3 + HCl$$

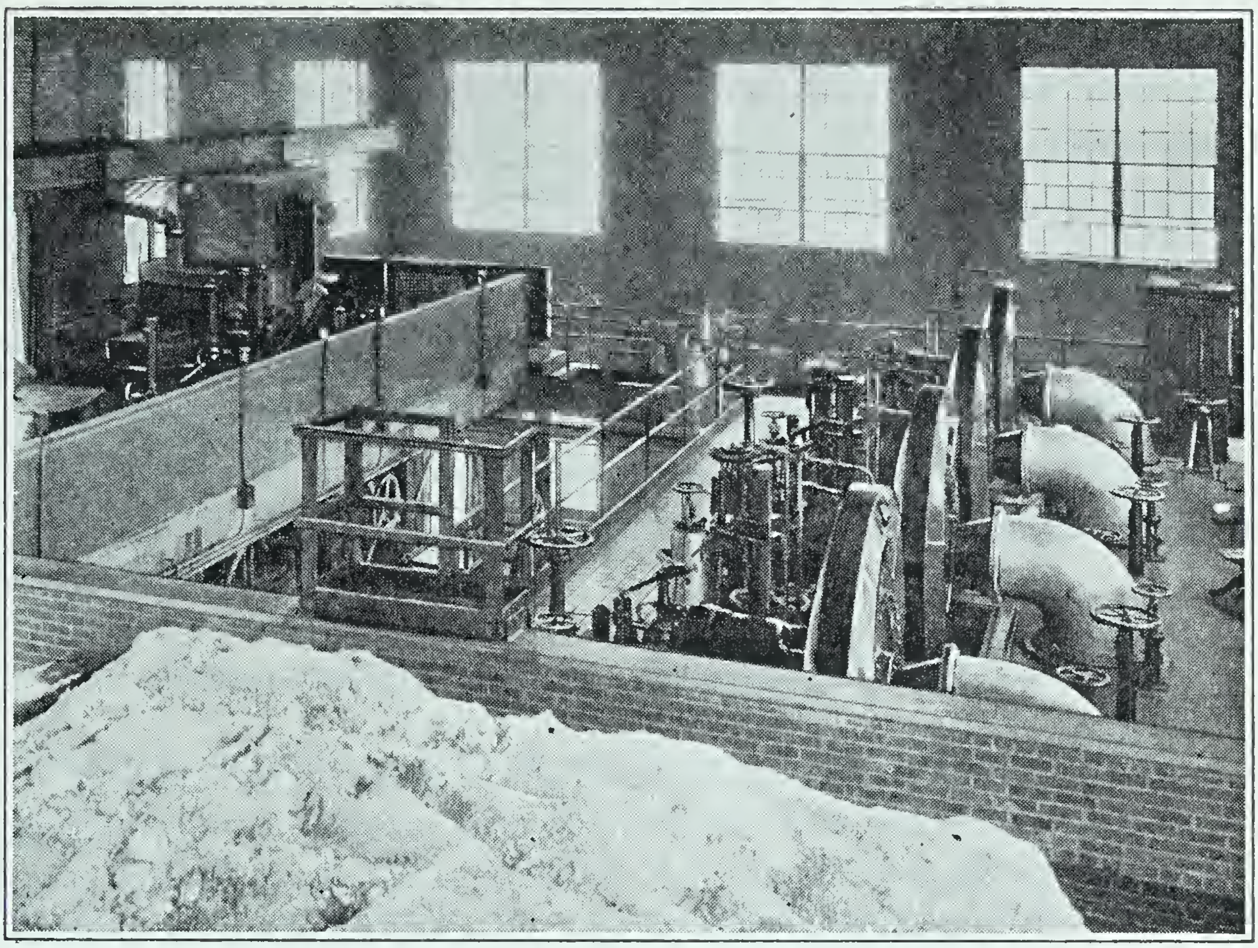


Fig. 211. Plant for the recovery of ammonium sulfate as a by-product in distilling coal. A large quantity of the recovered sulfate is in the foreground

It is used as a flux in soldering, in making dry cells, in medicine, and as a chemical reagent.

***Ammonium sulfate* (($NH_4)_2SO_4$).** This salt is especially valuable as a fertilizer. It is made by neutralizing sulfuric acid with ammonium hydroxide (Fig. 211).

Ammonium carbonates. There are two of these, namely, the normal salt, $(NH_4)_2CO_3$, and the acid salt, NH_4HCO_3. The normal carbonate is unstable, slowly giving off ammonia; so it is used in medicine under the name *smelling salts*. Both carbonates are valuable chemical reagents.

***Ammonium nitrate* (NH_4NO_3).** This is a rather unstable solid used as a constituent of certain explosives. It is also used in preparing the anesthetic called *laughing gas* (p. 302).

Ammonium sulfides. These are salts of hydrosulfuric acid (H_2S), commonly called hydrogen sulfide. Since the acid contains two replaceable hydrogen atoms, both the normal salt ($(NH_4)_2S$) and the acid salt (NH_4HS) are possible. Their solutions are used as reagents in testing for some of the metals.

Tests for ammonium salts. When any ammonium salt is warmed with sodium hydroxide, ammonia gas is given off. For example, with ammonium sulfate the reaction is as follows:

$$(NH_4)_2SO_4 + 2\ NaOH \longrightarrow Na_2SO_4 + 2\ H_2O + 2\ NH_3\uparrow$$

The ammonia evolved is easily recognized by its odor and by the fact that it will turn moistened red litmus paper blue. This makes a good test for ammonium salts, because no other salts give off ammonia under these conditions.

CHAPTER SUMMARY IN QUESTION FORM

1. In a general way, how do we get compounds of nitrogen?

2. (*a*) Name the two compounds that are used in preparing ammonia in the laboratory. (*b*) Write the equation for the reaction that takes place when these two compounds are heated together. (*c*) How is the ammonia given off collected?

3. (*a*) Mention the two principal sources of ammonia. (*b*) Which is the more important?

4. (*a*) What are the raw materials used in the Haber process? (*b*) Describe the chemistry involved in preparing ammonia by this process.

5. The following words apply to ammonia. Use them in a paragraph describing the gas:

lighter than
dissolves in
ammonium hydroxide
odor

6. Write the equation for the reaction that takes place when ammonia is brought in contact with water.

7. Name the chief uses of ammonia.

8. (*a*) In what proportion by volume do nitrogen and hydrogen unite to form ammonia? (*b*) How does the volume of ammonia formed by their union compare with the volumes of nitrogen and hydrogen that combined to form it? (*c*) What law does this illustrate?

9. (*a*) Describe the process of making artificial ice. (*b*) What are the properties of ammonia that make it useful in this process?

10. Define each of the following terms: (*a*) ammonia; (*b*) ammonium; (*c*) ammonium hydroxide; (*d*) aqua ammonia.

11. What are the chief household uses of aqua ammonia?

12. Neither water nor perfectly dry ammonia has any action on litmus paper, but a solution of ammonia in water turns red litmus blue. Explain.

13. (*a*) In general, what is the reaction between ammonium hydroxide and an acid? Illustrate your answer by writing the equations for the reactions between ammonium hydroxide and each of the following acids: (*b*) hydrochloric acid; (*c*) sulfuric acid; (*d*) nitric acid.

14. Give the names, formulas, and uses of three important ammonium salts.

15. Suppose you had a white solid that you thought might be an ammonium salt. How could you test it?

THOUGHT QUESTIONS

1. How does ammonia differ in properties from all other gases we have so far studied?

2. What would happen if you attempted to collect ammonia over water, as you did with oxygen and hydrogen?

3. In making artificial ice why is ammonia used rather than some other gas, such as carbon dioxide?

4. Is the principle involved in making artificial ice the same as in our household mechanical refrigerators (p. 60)?

5. Suppose you were to heat a mixture of sodium hydroxide and ammonium sulfate. Write the equation for the reaction that would take place.

6. What volume of ammonia could be obtained by heating 100 g of ammonium chloride with sodium hydroxide?

7. Name two compounds and two ions present in aqua ammonia.

8. Write the equations for the reactions showing how atmospheric nitrogen can be used in preparing ammonium sulfate.

OPTIONAL EXERCISES

1. Find out if there is an artificial-ice plant in your city or near your home. If one is available, visit the plant and write an account of the process as carried on there.

2. Ten liters of ammonia on decomposition would yield how many liters (*a*) of nitrogen? (*b*) of hydrogen?

CHAPTER XXVI

Nitric Acid and Its Salts, Long Known and of Great Importance; the Oxides of Nitrogen

Nitric acid (HNO_3) known to the alchemists. Nitric acid has long been known. As far back as the ninth century the alchemist Geber prepared nitric acid from one of its salts, potassium nitrate (KNO_3), commonly called *saltpeter*. The Germans still call the acid *Salpetersaure.* Today it is one of our important acids, both the acid and its salts having many uses. Two of its salts, sodium nitrate ($NaNO_3$) and potassium nitrate (KNO_3), are found in nature, and it is for this reason that the alchemists were familiar with them.

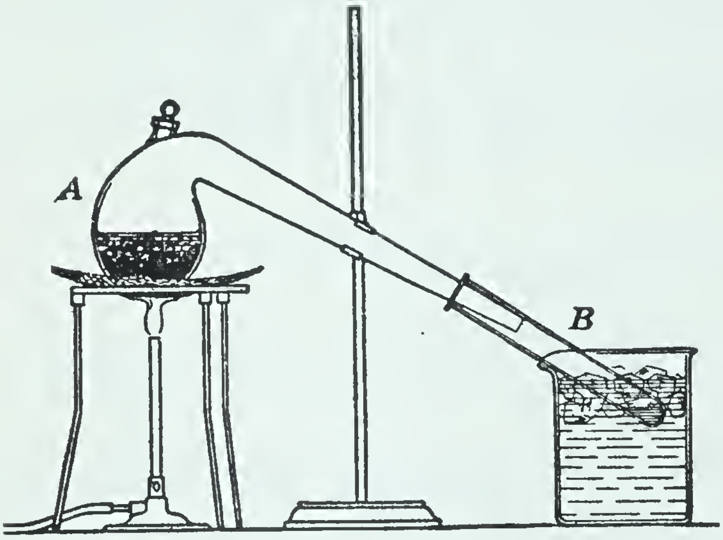


FIG. 212. Preparing nitric acid in the laboratory by the action of sulfuric acid on sodium nitrate

Hydrogen nitrate and nitric acid. Just as is true of all acids, if we wish to be very exact we must distinguish between the anhydrous compound HNO_3, called *hydrogen nitrate*, and nitric acid, which is a solution of hydrogen nitrate in water. Hydrogen nitrate itself is not often prepared, because it is so unstable; but its solution in water is easily obtained and is one of our most important acids. The concentrated nitric acid of commerce has a density of 1.4, and contains about 68 per cent of hydrogen nitrate and 32 per cent of water. When pure it is a colorless liquid, but it is often colored slightly yellow or brown by products of its decomposition.

Laboratory preparation of nitric acid. As a rule, nitric acid is prepared in the laboratory by the action of sulfuric acid on sodium nitrate ($NaNO_3$). When cold concentrated sulfuric acid is poured upon sodium nitrate, there is no visible chemical action. If, however, the mixture is gently heated in a retort *A* (Fig. 212), nitric acid is given off as a vapor. This can easily be condensed to a liquid by passing the vapor into a tube *B* surrounded by cold water. An examination of the liquid left in the retort shows that it contains sodium hydrogen sulfate ($NaHSO_4$), only one of the two atoms of hydrogen in sulfuric acid having been replaced by sodium. The reaction may be represented by the equation

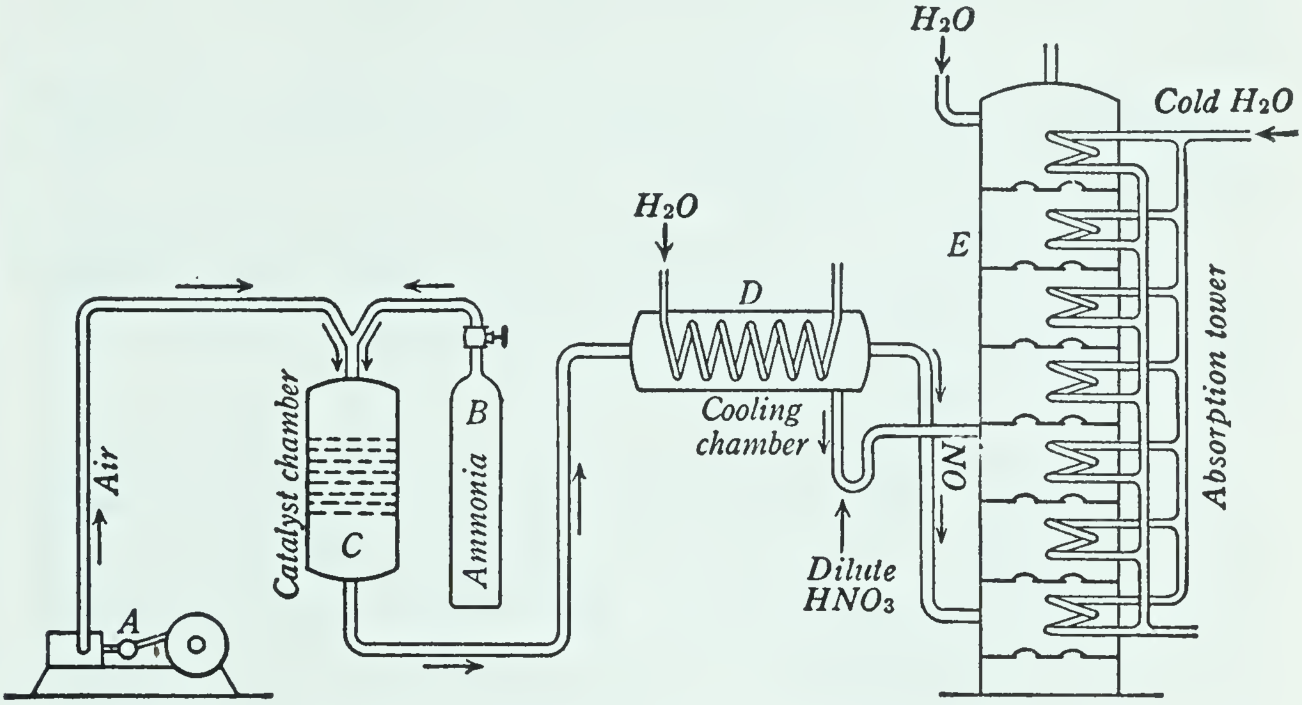


Fig. 213. Diagram of essential parts of apparatus used for preparing nitric acid on a large scale by oxidation of ammonia

A current of air (which furnishes the oxygen) and a current of ammonia enter the chamber *C*, which contains the catalyst. Here the ammonia is oxidized, forming oxides of nitrogen and nitric acid. These pass on through the cooling chamber *D* and enter the absorption tower *E*, where the action is completed. The nitric acid formed is withdrawn from the bottom of the tower

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3\uparrow$$

Commercial methods for getting nitric acid. Formerly all nitric acid was made commercially by the reaction just described. In recent years a new way has been developed, making use of nitrogen taken from the air; and this method has now largely replaced the older one. The process consists of two steps, as follows: (1) ammonia is made by the Haber process (p. 289); (2) a mixture of ammonia and air is then passed through tubes containing a suitable catalyst (platinum or iron oxide). In this step nitric acid is formed by the oxidation of the ammonia (Fig. 213). The reaction is very complex and really takes place in several steps, but the final results may be represented as follows:

$$NH_3 + 2\ O_2 \longrightarrow HNO_3 + H_2O$$

Chemical conduct of nitric acid. The important reactions of nitric acid are as follows:

1. ***Acid properties.*** Nitric acid has a large percentage of free ions in solution; so it is a strong acid. Like all other acids, it changes the color of indicators, and it reacts with bases to form salts.

2. ***Oxidizing action.*** Nitric acid is not so stable as hydrochloric acid. When heated, or when exposed for some time to sunlight, some of it decomposes, forming water and the two gases nitrogen dioxide (NO_2) and oxygen. Because of these facts *nitric acid is a good oxidizing agent.* As we go along we shall find that most acids are either oxidizing agents or reducing agents. Nitric acid has a peculiar action upon the skin, turning it yellow.

3. ***Action on metals.*** The way in which nitric acid acts on a metal depends on the position of the metal in the electromotive series (p. 261).

(*a*) *On metals above hydrogen.* With zinc (above hydrogen) we should expect nitric acid to set hydrogen free, just as does sulfuric acid:

$$Zn + 2\ H^+, NO_3^- \longrightarrow Zn^{++}, (NO_3^-)_2 + H_2\uparrow \qquad (1)$$

However, when we try the experiment, we get no hydrogen but, instead, another gas named nitric oxide (NO). It is easy to see the reason for this. Nitric acid is a strong oxidizing agent, while nascent hydrogen is an equally strong reducing agent. So any hydrogen set free according to equation (1) will be oxidized to water by the nitric acid:

$$3\ H + HNO_3 \longrightarrow 2\ H_2O + NO\uparrow \qquad (2)$$

If we study equations (1) and (2), we see that the products of the reaction between zinc and nitric acid are zinc nitrate, water, and nitric oxide. We may express this reaction in a single equation, as follows:

$$3\ Zn + 8\ HNO_3 \longrightarrow 3\ Zn(NO_3)_2 + 4\ H_2O + 2\ NO\uparrow \qquad (3)$$

(*b*) *On metals below hydrogen.* We do not expect a metal below hydrogen in the electromotive series to liberate hydrogen from an acid, but there is another possibility. The acid may oxidize the metal to form an *oxide.* This oxide may then dissolve in an excess of the acid to form a salt. With copper and nitric acid these two steps are represented in the following equations:

$$3\,Cu + 2\,HNO_3 \longrightarrow 3\,CuO + 2\,NO\uparrow + H_2O \qquad (1)$$

$$3\,CuO + 6\,HNO_3 \longrightarrow 3\,Cu(NO_3)_2 + 3\,H_2O \qquad (2)$$

Aqua regia. What reaction, if any, should we expect to take place when nitric acid and hydrochloric acid are mixed? Since nitric acid readily gives up oxygen, we should expect this oxygen to combine with the hydrogen of the hydrochloric acid, forming water and liberating nascent chlorine; and this is what slowly takes place:

$$HNO_3 + 3\,HCl \longrightarrow 2\,H_2O + NO\uparrow + 3\,Cl\uparrow$$

The mixture of nitric and hydrochloric acids was well known to the alchemists, who called it *aqua regia* ("royal water") because it dissolved gold, the king of metals. We still use this name.

Aqua regia is a very powerful solvent, not because it is an acid but *because it sets free nascent chlorine.* Metals (such as gold) which are not soluble in any common acid dissolve in aqua regia, forming complex compounds containing chlorine.

Uses of nitric acid. Nitric acid has countless uses in the industries and in chemical laboratories, and many thousands of tons are used every year in this country. It is most extensively used in the manufacture of explosives of various kinds and of celluloid, photographic films, and dyes.

Salts of nitric acid — nitrates. The salts of nitric acid are called *nitrates.* They are all solids soluble in water, and, when heated to a high temperature, undergo decomposition. The nitrates are most largely used in the manufacture of gunpowder and as fertilizers.

Sodium nitrate ($NaNO_3$). This salt, often called Chile saltpeter or simply nitrate, is found in nature in certain

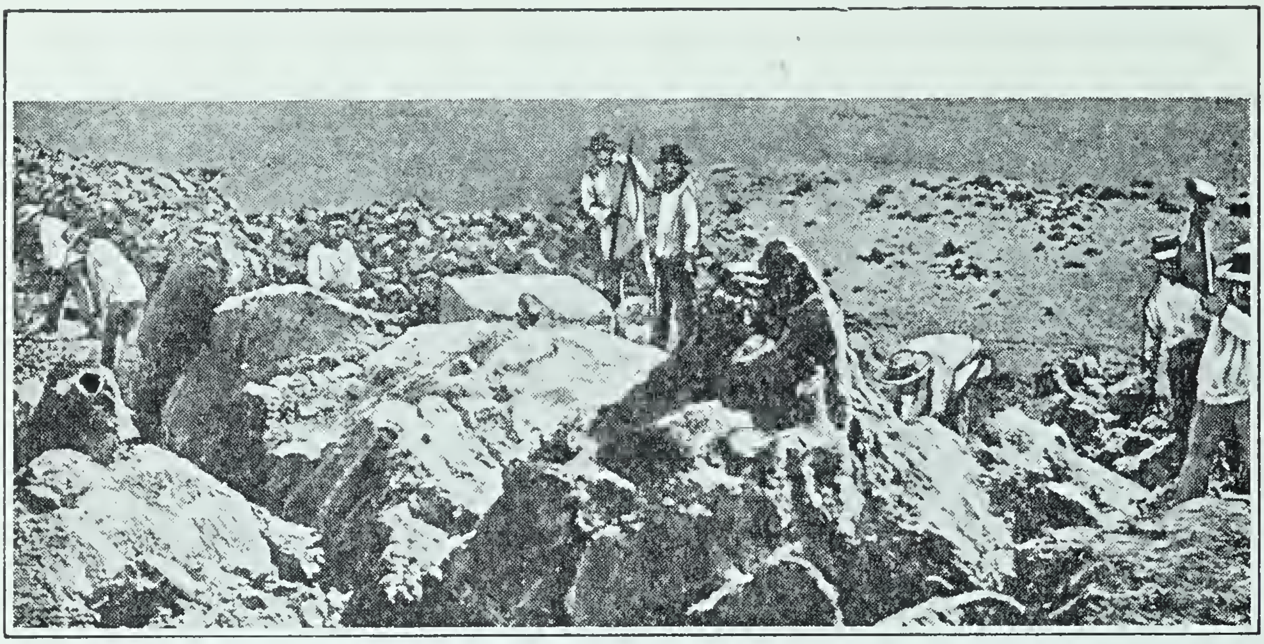


FIG. 214. A view of the deposits of sodium nitrate in Chile

desert regions where apparently it has been formed by the decay of organic substances in the presence of air and sodium salts. The largest deposits are in Chile (Fig. 214), and all the natural nitrate of commerce comes from that country. Smaller deposits occur in California and Nevada. The commercial salt is prepared by recrystallizing the crude nitrate (called *caliche*).

Potassium nitrate (KNO_3). This white salt, commonly called *saltpeter*, is formed in the decay of nitrogenous organic compounds, and so accumulates in some regions where the climate is hot and dry. At present it is prepared by the action of potassium chloride on sodium nitrate, both of which salts are found in nature in large quantities:

$$NaNO_3 + KCl \longrightarrow NaCl + KNO_3$$

It easily gives up its oxygen and so is a good oxidizing agent. Its chief use is in the manufacture of gunpowder.

Silver nitrate ($AgNO_3$). Silver nitrate, called *lunar caustic* by the alchemists, is made by dissolving silver in nitric acid, as the first step in making photographic plates and films (Fig. 215). It is a very soluble white solid. It can be cast into sticks and is used by surgeons to burn away small growths or proud flesh, which gives it the name *caustic*.

Gunpowder; blasting powder. Gunpowder is a mixture of finely divided sulfur, charcoal, and either potassium nitrate or sodium nitrate. Potassium nitrate is more expensive,

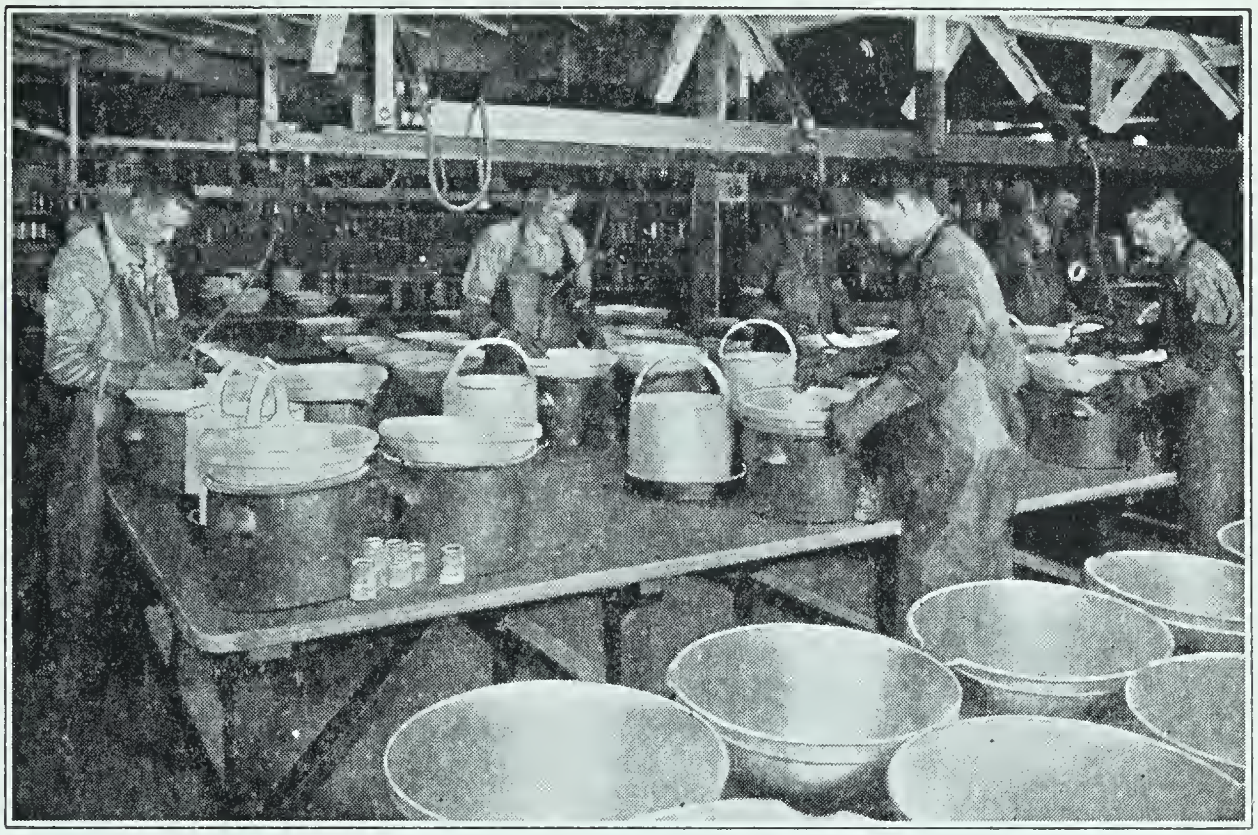


FIG. 215. Preparing silver nitrate by dissolving silver in nitric acid. Large quantities of the nitrate are used in preparing compounds needed in photography

but is better because sodium nitrate is deliquescent and attracts moisture from the air. When sodium nitrate is used, the explosive is known as *blasting powder*. It must be kept in airtight containers until ready for use.

When the gunpowder is ignited, complicated reactions take place, and a number of different products are formed, the chief of which are the gases carbon dioxide, carbon monoxide, and nitrogen, and the solids potassium carbonate, sulfate, and sulfide. It is not nearly so powerful as some other explosives that will be described later.

Test for nitrate ions. When nitric acid is added to a solution of ferrous sulfate ($FeSO_4$), an intensely brownish-black color appears. The reaction is not a simple one, but it is used as an easy test for the presence of a nitrate or of nitric acid (each gives the nitrate ion, NO_3^-). The test is made as follows:

To a solution in a test tube, suspected of containing nitrate ions, is added a solution of ferrous sulfate. Concentrated sulfuric acid is then carefully poured into the test tube (held in a slanting position) in such a way as to run down the inside of the tube and collect on the bottom without mixing with the solution. If nitrate ions are present, a brown ring forms between the heavy sulfuric acid and the lighter solution (containing the nitrate ions) floating on top.

Nitrous acid (HNO_2). It is an easy matter to obtain sodium nitrite ($NaNO_2$) by heating sodium nitrate with lead:

$$NaNO_3 + Pb \longrightarrow NaNO_2 + PbO$$

Now when sodium nitrite is treated with an acid, such as sulfuric acid, it is decomposed, and nitrous acid is set free:

$$NaNO_2 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_2$$

But the acid is very unstable and at once decomposes into water and oxides of nitrogen. Sodium nitrite is used in the manufacture of dyes.

Illustration of oxidation and reduction. In the reaction of sodium nitrate with lead we have a good example of oxidation and reduction. It is evident that lead has gained oxygen (oxidation), and sodium nitrate has lost oxygen (reduction).

Thinking of the reaction as an exchange of electrons (p. 207), we see that a lead atom loses 2 valence electrons (oxidation) and an oxygen atom gains 2 valence electrons (reduction). The result is the electrovalent compound $Pb^{++}, :\ddot{\underset{..}{O}}:^{--}$.

OXIDES OF NITROGEN

NAME	FORMULA	DESCRIPTION
Nitrous oxide	N_2O	A colorless gas
Nitric oxide	NO	A colorless gas
Nitrogen dioxide	NO_2	A reddish-brown gas
Nitrogen trioxide	N_2O_3	Known only at low temperatures
Nitrogen pentoxide	N_2O_5	A white solid

Nitrous oxide (laughing gas) (N_2O). The easiest way to get this gas is by heating ammonium nitrate:

$$NH_4NO_3 \longrightarrow 2\ H_2O + N_2O\uparrow$$

It is colorless, is somewhat soluble in water, and in solution has a slightly sweetish taste. When inhaled it produces a kind of hysteria (hence the name *laughing gas*) and, if breathed in larger amounts, unconsciousness and insensibility to pain. These properties were discovered by young

Humphry Davy (Fig. 163), and for a time it was a social fad to enliven parties by its use. It was the first substance to be employed as an anesthetic in surgery; and it is still used in minor operations, such as those of dentistry (Fig. 216), and even in more serious ones.

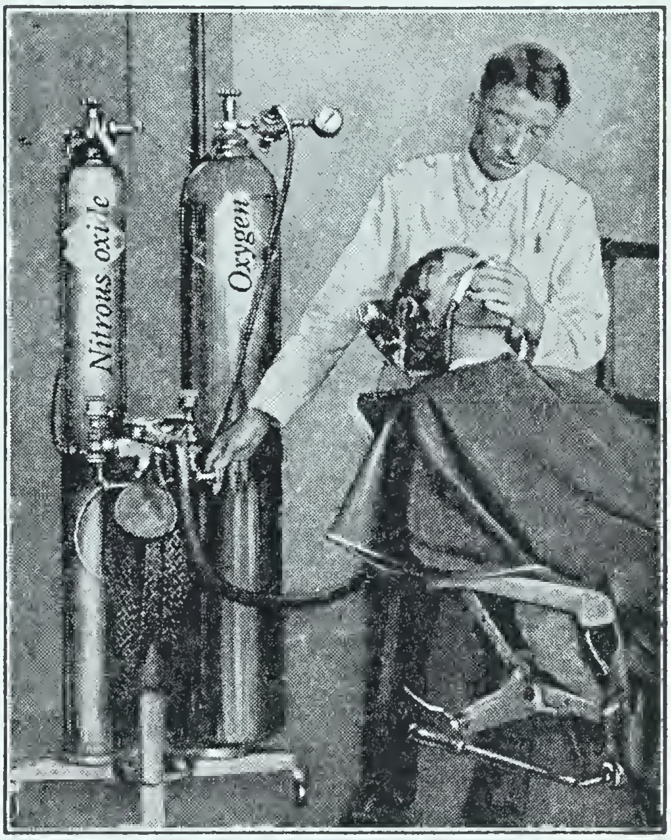


Fig. 216. Administering laughing gas mixed with oxygen in a dental operation

Nitrous oxide is a very energetic oxidizing agent. Substances such as carbon, sulfur, iron, and phosphorus burn in it almost as brilliantly as in oxygen, forming oxides and setting free nitrogen. Evidently the oxygen in nitrous oxide is not held in very firm combination by the nitrogen.

Nitric oxide (NO). Nitric oxide is most conveniently made by the action of nitric acid upon copper (Fig. 217):

$$3\,Cu + 8\,HNO_3 \longrightarrow 3\,Cu(NO_3)_2 + 4\,H_2O + 2\,NO\uparrow$$

Lightning discharges cause the union of oxygen and nitrogen in the air to form some of the oxide. It is a colorless, poisonous gas, and, unlike nitrous oxide, does not give up its oxygen readily to act as an oxidizing agent. The flames of burning substances introduced into the gas usually are extinguished.

Nitrogen dioxide (NO_2). When nitric oxide comes into contact with oxygen or air, it at once combines with the oxygen even at room temperatures (Fig. 218), forming *nitrogen dioxide* (NO_2):

$$2\,NO + O_2 \longrightarrow 2\,NO_2$$

It is a reddish-brown gas of unpleasant odor, and is very poisonous when inhaled.

Acid anhydrides. The oxides N_2O_3 (nitrogen trioxide) and N_2O_5 (nitrogen pentoxide) are rarely prepared, and so they will not be separately described. They bear a very interesting relation to the acids of nitrogen. When dissolved in water these oxides combine with the water, forming acids. To some extent this is true of carbon dioxide, CO_2 (p. 153).

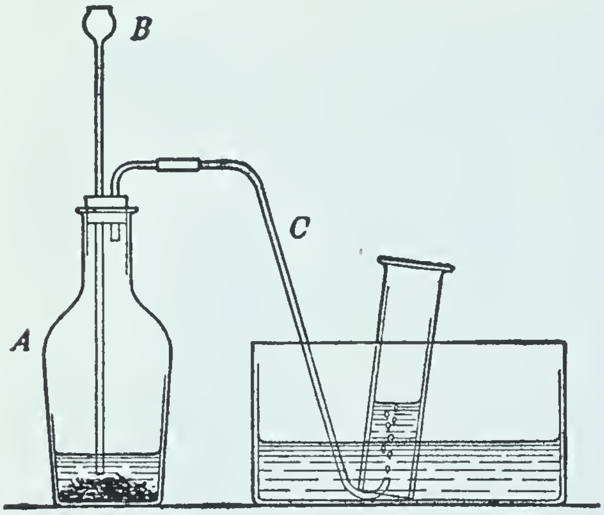


Fig. 217. Preparation of nitric oxide

Copper turnings are placed in the bottle *A* and nitric acid is added through the funnel tube *B*. Nitric oxide escapes through *C* and is collected over water

$$N_2O_3 + H_2O \longrightarrow 2\ HNO_2 \text{ (nitrous acid)}$$
$$N_2O_5 + H_2O \longrightarrow 2\ HNO_3 \text{ (nitric acid)}$$
$$CO_2 + H_2O \longrightarrow H_2CO_3 \text{ (carbonic acid)}$$

In each case the oxide is called the *anhydride* of the corresponding acid. *An acid anhydride is an oxide whose combination with water forms an acid.* N_2O_3 is called nitrous anhydride; N_2O_5 is nitric anhydride; CO_2 is carbonic anhydride. We shall meet with many other acid anhydrides as we continue our study.

Basic anhydrides. In a similar way, *a basic anhydride is an oxide whose combination with water forms a base.* Na_2O and CaO, for example, are basic anhydrides:

$$Na_2O + H_2O \longrightarrow 2\ NaOH$$
$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Metals and nonmetals. In succeeding chapters we shall often want to speak of metals and nonmetals. Having in mind the distinction between anhydrides of acids and of bases we may make a partial definition as follows: *A metal is an element whose oxide is a basic anhydride; a nonmetal is an element whose oxide is an acid anhydride.* Sodium and calcium are examples of metals; nitrogen and carbon, of nonmetals.

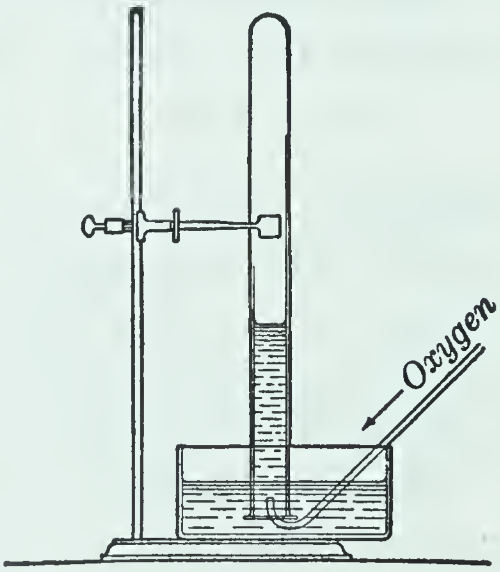


Fig. 218. The formation of nitrogen dioxide from nitric oxide and oxygen

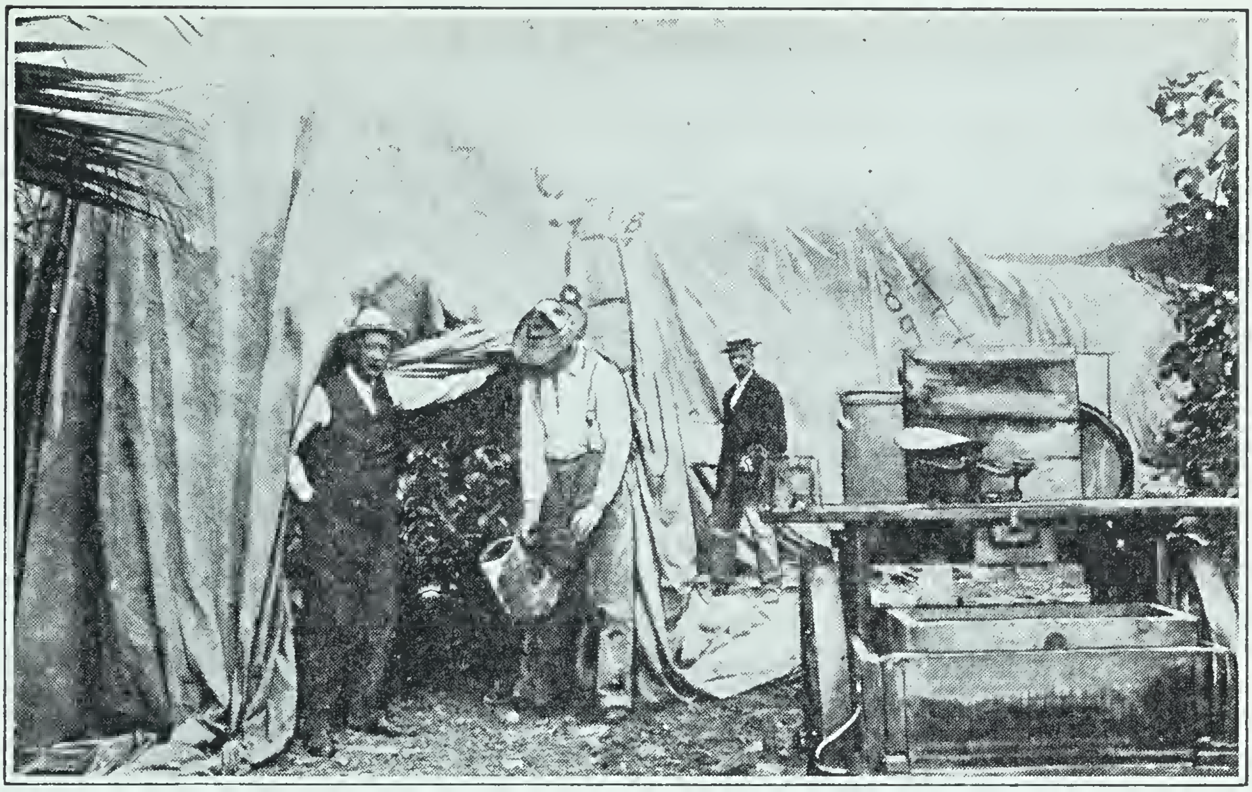


FIG. 219. Fruit trees covered with canvas, under which hydrogen cyanide is being liberated to kill insect pests

COMPOUNDS OF NITROGEN WITH CARBON

Cyanogen (C_2N_2); hydrogen cyanide (HCN) (or hydrocyanic acid). At high temperatures carbon unites with nitrogen to form the colorless, very poisonous gas known as cyanogen (C_2N_2). With hydrogen and nitrogen it forms hydrogen cyanide (HCN), a colorless liquid boiling at 26°. The group CN acts as a univalent radical in all cyanide compounds. Hydrogen cyanide vapor has the odor of peach kernels. *It is one of the most poisonous compounds known,* and is used to destroy insects, especially those on citrus fruit trees, such as lemon and orange trees (Fig. 219).

When dissolved in water, hydrogen cyanide forms a *very weak* acid called *hydrocyanic acid* or *prussic acid.* Its salts are called *cyanides.* Sodium cyanide (NaCN) is a white solid; its solution dissolves gold and is used in getting gold from its ores. It is also used to kill butterflies and beetles for museum collections. Potassium cyanide (KCN) is very much like sodium cyanide. *All cyanides, as well as the free acid, are very poisonous.* When a cyanide is treated with sulfuric acid, hydrogen cyanide is formed:

$$NaCN + H_2SO_4 \longrightarrow NaHSO_4 + HCN\uparrow$$

CHAPTER SUMMARY IN QUESTION FORM

1. Distinguish between *hydrogen nitrate* and *nitric acid.*

2. Give the laboratory method for preparing nitric acid, writing the equation for the reaction involved.

3. (*a*) Give the two methods for preparing nitric acid commercially. (*b*) Which one is more largely used?

4. Aside from its acid properties, what is the chief characteristic of nitric acid?

5. (*a*) Explain the action of nitric acid on metals above hydrogen in the electromotive series; (*b*) on metals below hydrogen in the series.

6. (*a*) What name is given to a mixture of hydrochloric acid and nitric acid? (*b*) Account for the fact that while neither hydrochloric acid nor nitric acid will dissolve gold, yet a mixture of the two will dissolve it.

7. (*a*) What name is given to the salts of nitric acid? (*b*) Mention three properties common to such salts.

8. (*a*) Give the names and formulas of three common salts of nitric acid. (*b*) What is the source of each? (*c*) Give the chief use of each.

9. (*a*) What are the main constituents of common gunpowder? (*b*) Why is potassium nitrate to be preferred to sodium nitrate as a constituent of gunpowder?

10. (*a*) What compounds give the NO_3^- ion in solution? (*b*) Give the common test for the NO_3^- ion.

11. Distinguish between *nitrous acid* and *nitrites.*

12. Give the names and formulas for the oxides of nitrogen.

13. (*a*) Give two names for the compound that has the formula N_2O. (*b*) How is it prepared? (*c*) For what is it used?

14. Copper is dissolved in nitric acid. (*a*) What becomes of the copper? (*b*) What gas is evolved? (*c*) What compound forms when this gas comes in contact with the air?

15. What name is given to oxides (*a*) that combine with water to form acids? (*b*) that combine with water to form bases?

16. (*a*) Which of the following oxides are acid anhydrides, and which basic anhydrides: N_2O_3, N_2O_5, CO_2, CaO? (*b*) Write the equations for the reactions between each of these oxides and water, giving the names of each of the compounds formed.

17. What compound does nitrogen form (*a*) with carbon? (*b*) with hydrogen and carbon?

18. (*a*) Distinguish between cyanogen, hydrogen cyanide, hydrocyanic acid, and prussic acid. (*b*) What property have all of these in common?

19. (*a*) What name is given to the salts of hydrocyanic acid? (*b*) What gas is evolved when a cyanide such as sodium cyanide is treated with sulfuric acid?

20. (*a*) What is the chief use of hydrocyanic acid? (*b*) of sodium cyanide?

21. Why must we be *extremely careful* when working with hydrocyanic acid or its salts?

THOUGHT QUESTIONS

1. What compounds are formed when an electric discharge is passed through a mixture (*a*) of nitrogen and hydrogen? (*b*) of nitrogen and oxygen?

2. What is the source of each of the elements present in the ordinary nitric acid of commerce?

3. What substances have we studied that might be formed during lightning storms?

4. What gas is evolved when zinc is dissolved (*a*) in hydrochloric acid? (*b*) in dilute sulfuric acid? (*c*) in nitric acid? (*d*) Account for any difference in the gas evolved.

5. Which of the following statements are true and which are false? (*a*) All nitrates are soluble. (*b*) Ammonia is a base. (*c*) Nitrous oxide is an anesthetic. (*d*) The nitrogen present in nitric acid prepared on a commercial scale comes from the atmosphere. (*e*) All the oxides of nitrogen are colorless gases. (*f*) Nitrous oxide supports combustion.

6. Give the formula and chemical name for each of the following: (*a*) saltpeter; (*b*) Chile saltpeter; (*c*) lunar caustic; (*d*) caustic soda; (*e*) caustic potash; (*f*) laughing gas; (*g*) marble; (*h*) muriatic acid; (*i*) dry ice; (*j*) carbonic acid gas; (*k*) oil of vitriol.

7. How should you proceed to find out whether the formula for cyanogen is C_2N_2 or CN?

8. Which contains the greater weight of oxygen, (*a*) 100 g of potassium chlorate or (*b*) 100 g of potassium nitrate?

9. Suppose you had five bottles filled, respectively, with ammonia, nitric oxide, nitrous oxide, carbon dioxide, and hydrogen. How could you distinguish any one from the others?

OPTIONAL EXERCISES

1. Show by diagrams how it happens that 3 volumes of hydrogen and 1 volume of nitrogen, on combining, form only 2 volumes of ammonia.

2. The concentrated nitric acid of commerce has a density of 1.4 and contains (approximately) 68 per cent of hydrogen nitrate. Suppose you wished to prepare 1 liter of this acid. What weights of (*a*) sodium nitrate and (*b*) hydrogen sulfate would be required?

3. (*a*) What is the formula of ammonium nitrite? (*b*) of ammonium nitrate? Suppose you were to heat 10 g of each separately. (*c*) What gases would be given off in each case (pp. 268, 302), and what weight of each?

CHAPTER XXVII

Reversible Reactions; Equilibrium

[Reactions That Go in Either Direction]

Introduction. If we start the engine of an automobile and throw in one set of gears, the car moves forward; if we shift gears, it reverses its direction and moves backward. The car can go forward or backward; but it cannot move in both directions at the same time, *because it is an individual.*

If we watch the cars passing in the street, we at once see that they *are* going in opposite directions at the same time, *because there are numbers of them.* Each individual car goes one way only, but taken all together they are going in both directions.

If we are interested in some one thing about the cars passing in the street, — their direction, their color, their make, their number of cylinders, — we shall soon stop marking the numbers in actual figures and express them in percentages. *On the average,* 40 per cent go in one direction and 60 per cent in the opposite direction; or 50 per cent are black, 50 per cent are colored. In regard to the latter we could further work out the percentage of each of the various colors. These results would be called *statistical.* They would be *average* figures for a very large number of individual cases.

Now we reason in this same way about molecules as well as about motor cars. The chemist is rarely concerned with the *individual* molecules in a reaction but with vast numbers of them; so all his calculations about molecules taking part in a reaction are statistical and not individual.

Reversible reactions. In a number of cases we have studied reactions that were said to be able to go in either direction. For example, in the Haber process, nitrogen and hydrogen combine to form ammonia, but at the same time ammonia decomposes more or less rapidly into nitrogen and hydrogen.

$$N_2 + 3\,H_2 \rightleftarrows 2\,NH_3$$

This does not mean that the reaction first goes one way for a time and then reverses, as a single automobile would do or as the pendulum of a clock swings. It means that, in a mixture of nitrogen, hydrogen, and ammonia, molecules of nitrogen and hydrogen are here and there reacting to form ammonia while at the same time molecules of ammonia are here and there decomposing. In automobile language, there is two-way traffic, represented by the double arrow ($\rightleftarrows$).

Similarly, when we dissolve ammonia in water, ammonium hydroxide is formed, which readily decomposes again into ammonia and water (p. 292):

$$NH_3 + H_2O \rightleftarrows NH_4OH$$

Reactions of this kind, which can go in either direction or in both directions at the same time, are called "reversible reactions." Many physical changes are of this reversible kind, such as the evaporation of water in a closed space:

$$\text{Liquid water} \rightleftarrows \text{water vapor}$$

Objections. One might be inclined to argue that if, in a mixture of nitrogen and hydrogen, conditions are favorable for *any* molecules of the two gases to unite, they would be favorable for *all* molecules. There would then be no reason for ammonia molecules to decompose into nitrogen and hydrogen and at once unite again.

This reasoning would be sound *if all the molecules in the gas mixture were under the same conditions.* But they are not. Some are moving with the speed of a rifle bullet, some very slowly; some are in violent collision, some in gentle collision, while some escape collision for a time. So it is not very surprising that in a gas mixture some molecules are being formed, while others are being knocked to pieces.

Equilibrium. If now we prepare a mixture of substances capable of taking part in a reversible reaction, and allow the reaction to go on for a time, it is evident that the two opposite reactions will presently become so adjusted to each other that *the changes in the one direction will just offset those in the other direction.* This balanced state of affairs is called *equilibrium.* The individual molecules will keep on reacting with each other, but in a statistical way the *average percentage* of each substance present will remain unchanged.

Let us suppose that in a reversible reaction an equilibrium has been reached. Now if the conditions under which the reaction is carried out are changed, the point of equilibrium will also change, and a new one will be set up. For example, in the Haber process for preparing ammonia the percentage of ammonia present when equilibrium is reached may vary all the way from 5 or 6 to more than 90, depending upon the catalyst used and the temperature and pressure under which the reaction is carried out.

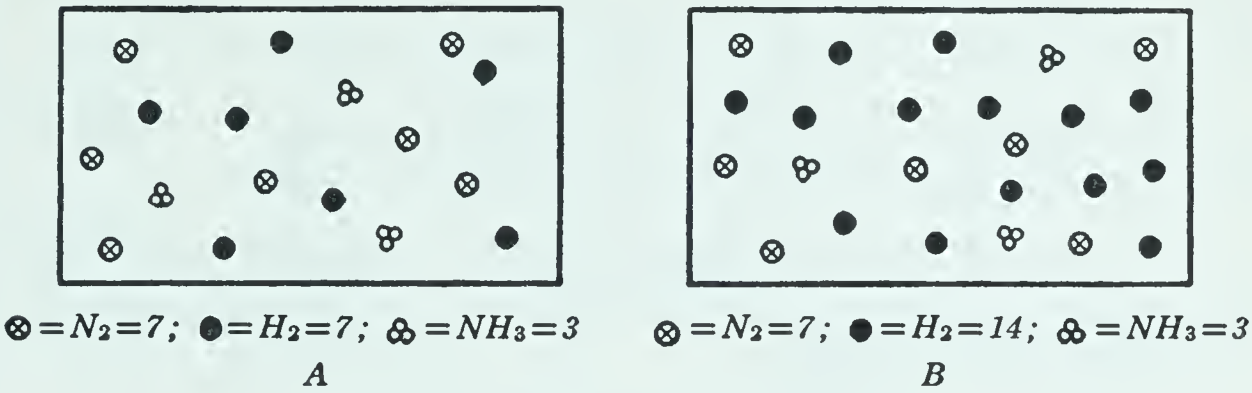

⊗ = N_2 = 7; ● = H_2 = 7; ∴ = NH_3 = 3
A
⊗ = N_2 = 7; ● = H_2 = 14; ∴ = NH_3 = 3
B

FIG. 220. Graphic illustration of mass action

In *A* the chances for one molecule of nitrogen to meet three molecules of hydrogen to form more ammonia are not very good. In *B*, with twice as many molecules of hydrogen as in *A*, the chances for meeting are much better, and a larger percentage of ammonia will begin to form

Mass action. Let us suppose that in the Haber process the equilibrium between nitrogen, hydrogen, and ammonia is reached as represented in the equation

$$\underset{(25.3\%)}{N_2} + \underset{(54.7\%)}{3\ H_2} \rightleftarrows \underset{(20\%)}{2\ NH_3}$$

What will happen if we now add more of any one of these three gases to the mixture?

If we add either hydrogen or nitrogen, it will not greatly change the rate at which ammonia is decomposing; for this does not depend on the other gas. But it *will increase* the rate at which hydrogen and nitrogen are combining; for an excess of either one causes the two kinds of molecules to meet oftener and so have a chance to combine (Fig. 220, *B*). This will shift the equilibrium toward a greater percentage of ammonia than in Fig. 220, *A*. If we add both hydrogen and nitrogen in the ratio in which they are present at equilibrium, there will be no change in the equilibrium percentages.

If we add ammonia to the equilibrium mixture, there will be many more molecules of it to decompose, while they will be forming at nearly the same old rate. So the equilibrium will come back to about its original figure.

The change in the point of equilibrium caused by an excess of one of the reacting materials is called mass action.

The equilibrium of nitrogen dioxide. At moderately high temperatures nitrogen dioxide begins to decompose in accordance with the equation

$$2\ NO_2 \rightleftarrows 2\ NO + O_2$$

An excess of either oxygen or nitric oxide will diminish the percentage of this decomposition at any given temperature.

Bringing reversible reactions to completion. In the laboratory as well as in manufacturing operations we want to get as large a yield as possible from the materials we use. So we avoid a reaction that results in an equilibrium. If we cannot find such a reaction, we hunt for ways to break up the condition of equilibrium and bring the reaction to completion. Again in automobile language, we want to bring about one-way traffic.

If, in a reversible reaction, we can so arrange conditions that *one product of the reaction is removed as fast as it is formed*, there can be no reverse reaction and no equilibrium. The reaction will then go on to completion. For example, in the Haber process (p. 289) we circulate the reaction mixture over water or sulfuric acid, *which removes the ammonia molecules as fast as they are formed*; and the reaction mixture can then produce more ammonia.

A reversible reaction may be changed into a completed reaction by removing one of the substances taking part in it as fast as it is formed.

Let us take another example. Ordinary limestone is impure calcium carbonate ($CaCO_3$). When heated it decomposes into the solid called lime (CaO) and the gas carbon dioxide. If it is heated in a *closed* vessel (Fig. 221), where nothing can get away, equilibrium is soon reached:

$$CaCO_3 \rightleftarrows CaO + CO_2\uparrow$$

But if the vessel is *open* the carbon dioxide escapes as fast as it is formed, and the reaction goes to completion (Fig. 222).

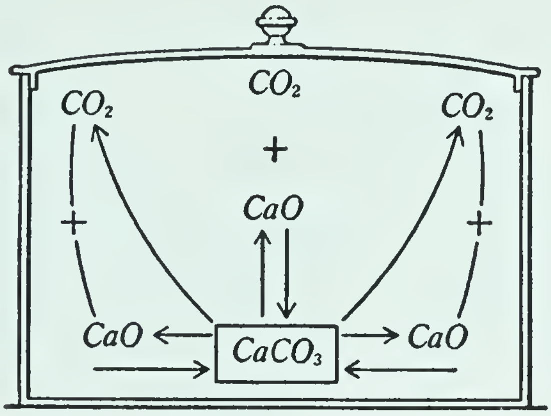


Fig. 221. Limestone heated in a closed vessel

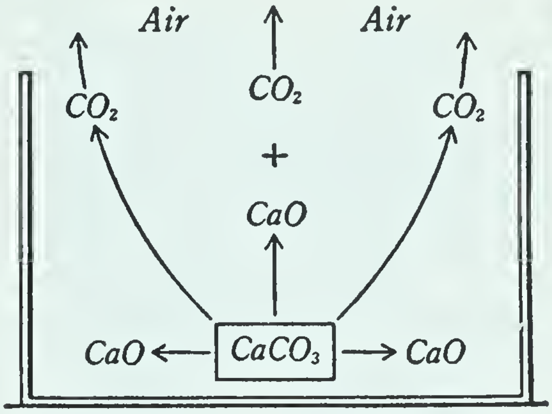


Fig. 222. Limestone heated in an open vessel

Equilibrium among ions. In our study we shall be dealing chiefly with electrolytes in solution, that is, with their *ions.* And if several electrolytes are in a solution together, there will be quite a variety of ions present. An equilibrium among some of these ions may take place in either of two ways:

1. ***Equilibrium between ions and a solid crystal.*** As a solution becomes concentrated, any pair of ions that form a sparingly soluble solid will begin to build themselves into solid crystals and so, in part, leave the solution. There will then be an equilibrium between the solid crystals and their ions remaining in solution. For example, *at saturation* we may have the equilibrium

$$\mathrm{Na^+ + Cl^- \rightleftarrows NaCl\downarrow}$$

2. ***Equilibrium between free and bound ions.*** In other cases, as concentration increases, more and more of the ions pass into the inactive state, and there is equilibrium between the free and the bound ions. For example, in concentrated nitric acid we have the equilibrium

$$\mathrm{H^+, NO_3^- \rightleftarrows \overline{H^+, NO_3^-}}$$

3. ***Equilibrium between ions and a covalent compound.*** Sometimes two oppositely charged ions unite to share their valence electrons, and so form a covalent compound. In neutralization we have the equilibrium

$$\mathrm{K^+, OH^- + H^+, Cl^- \rightleftarrows K^+, Cl^- + H:OH,}$$

in which *almost all* the H^+ ions and OH^- ions have united to form water, expressed by the covalent formula H : OH.

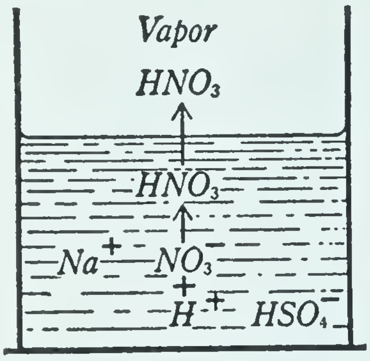


Fig. 223. Preparation of nitric acid

Completion of reactions between ions. For the most part the chemist works with ion reactions in solution or in melted mixtures. So he is especially interested in finding out how to bring reversible reactions of this kind to completion. He has found that *three general conditions may be depended on to bring a reversible reaction between ions to completion.*

1. ***A pair of ions may form a covalent gas and escape.*** If the reaction goes on under such conditions that one of the products is a *gas insoluble in the solvent,* the gas will make its escape as fast as it is formed. The reaction will then continue until one or the other of the ions taking part in it is used up.

For example, when we mix sulfuric acid and sodium nitrate (Fig. 223), no visible reaction takes place at room temperature. But if we heat the mixture above the boiling point of nitric acid, then the nitric acid formed in the equilibrium between the H^+ and the NO_3^- ions is converted into a gas *insoluble in sulfuric acid* and distills away until the NO_3^- ions are used up. We then have a completed reaction expressed in the equation

$$Na^+, NO_3^- + H^+, HSO_4^- \longrightarrow Na^+, HSO_4^- + HNO_3\uparrow$$

In the preparation of hydrogen chloride (p. 226) we have the completed reaction

$$Na^+, Cl^- + H^+, HSO_4^- \longrightarrow Na^+, HSO_4^- + HCl\uparrow,$$

because even at room temperature hydrogen chloride is a gas insoluble in sulfuric acid (Fig. 161). *It is in this way that most acids are prepared.* Most of them are rather low-boiling liquids. Their salts are heated *with some acid of high boiling point,* usually with sulfuric acid, which boils at 338°.

2. ***A pair of ions may form (nearly) insoluble crystals and precipitate.*** When hydrochloric acid (HCl) and silver nitrate ($AgNO_3$) are brought together in solution, we have the ions

H^+, Cl^-, Ag^+, NO_3^-. Now silver chloride ($AgCl$) *is insoluble in water or acids.* So the Ag^+ ions and the Cl^- ions at once build themselves into the (insoluble) solid $AgCl$, and precipitate as a curdy white solid. The reaction will go on until one or the other of these ions is almost entirely used up (Fig. 224). The reaction may be written

$$Ag^+, NO_3^- + H^+, Cl^- \longrightarrow H^+, NO_3^- + AgCl\downarrow$$

In a similar way we have the reaction

$$Ba^{++}, Cl^-{}_2 + H^+{}_2, SO_4^{--} \longrightarrow 2\,H^+, Cl^- + BaSO_4\downarrow$$

because barium sulfate ($BaSO_4$) is insoluble in water and acids.

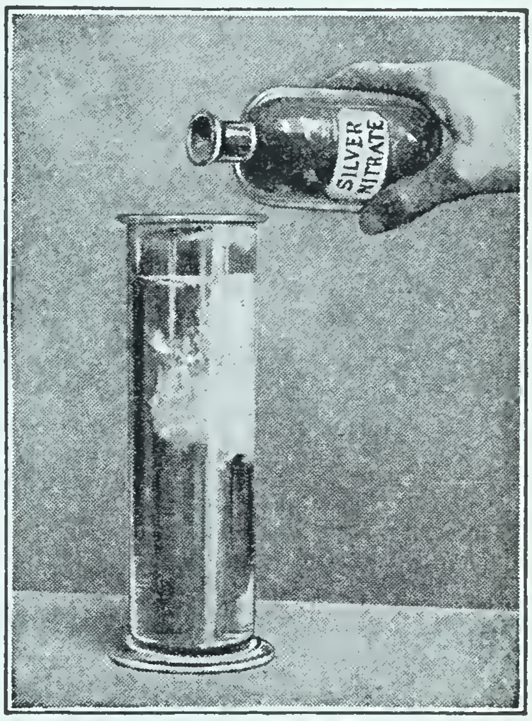


Fig. 224. Precipitating silver chloride by the action of silver nitrate on hydrochloric acid

3. ***A pair of ions may unite to form an un-ionized (covalent) molecule.*** When we bring together sodium hydroxide and hydrochloric acid in solution, we have the ions H^+, Cl^-, Na^+, and OH^-. The H^+ ions and the OH^- ions unite to form molecules of water *which do not again part into ions* save to a very slight extent. This leaves only the ions of $NaCl$ in solution, the equation being

$$Na^+, OH^- + H^+, Cl^- \longrightarrow Na^+, Cl^- + H:OH$$

Neutralization is practically a completed reaction, *because water is so little ionized*; and when the ions OH^- and H^+ unite to form a water molecule, they are *almost* completely removed from taking further part in a reaction.

The test for chloride and carbonate ions. From what has been explained under 2 above, it is evident that the test described for hydrochloric acid and the chlorides (p. 227) is really a test for chloride *ions*. It is equally true that the test for carbon dioxide (p. 153) is really a test for the carbonate ion CO_3^{--} derived from the ionization of carbonic acid, rather than a direct test for CO_2 molecules.

Normal solutions. A normal (N) solution of an *acid* is one that contains 1 gram-ion weight of H^+ ions per liter (1.008 g); and a normal solution of a *base* contains 1 gram-ion weight of OH^- ions per liter (17.008 g). A tenth-normal solution of an acid (expressed as $N/10$ or 0.1 N) contains 1.008/10 g of H^+ ions, and a one-thousandth-normal solution (0.001 N) contains 1.008/1000 g. In the same way a one-thousandth-normal base contains 17.008/1000 g of OH^- ions.

***p*H value: Hydrogen-ion concentration.** Now pure water contains *minute* but *equal* concentrations of *both* H^+ ions and OH^- ions, due to the equilibrium

$$H_2O \rightleftarrows H^+ + OH^-$$

Exact measurements show that in pure water the H^+ concentration is 0.0000001 N. This, and similar H^+ concentrations, can be represented in a much more convenient way as follows: The symbol *p*H is chosen to indicate the concentration of the ion. It states the *number of zeros plus the first significant figure* that follow the decimal point of the N concentration. Thus the number 0.0000001 N is represented by $p\mathrm{H} = 7$. Acidity of 0.0001 N is $p\mathrm{H} = 4$; 0.00001 N is $p\mathrm{H} = 5$. If a little acid is added to water the normal value becomes *greater*, and the *p*H value is *less* than 7. If the *p*H is greater than 7, the solution is alkaline. While such concentrations are very small, they are of great importance in physiology and in many industries.

CHAPTER SUMMARY IN QUESTION FORM

1. What name do we give to a reaction that goes in either direction?

2. What name do we apply to the condition that exists in a reaction when the change in the one direction just equals the change in the other?

3. To show how we represent a reversible reaction, write the equation (*a*) for the preparation of ammonia by the Haber process; (*b*) for the reaction between ammonia and water; (*c*) for the reaction between sodium chloride and the ions it forms when dissolved in water.

4. Suppose in the reaction represented by the equation

$$N_2 + 3\ H_2 \rightleftarrows 2\ NH_3$$

an equilibrium exists. What would be the effect of increasing (*a*) the amount of hydrogen present? (*b*) the amount of nitrogen present?

5. What term do chemists apply to the change in the point of equilibrium brought about by adding an excess of one of the reacting materials?

6. When heated in an open retort limestone is completely decomposed into calcium oxide and carbon dioxide, but it is not completely decomposed if the retort is closed. Explain.

7. (*a*) Is it possible in all reversible reactions taking place in solutions to bring the reaction to completion? (*b*) Name three conditions which, if they exist, will enable you to bring the reaction to completion.

8. When sodium nitrate is heated with sulfuric acid, the reaction goes to completion. Why?

9. When a solution of silver nitrate is added to hydrochloric acid, the reaction goes to completion. (*a*) Why? (*b*) Give the name and formula for each compound formed.

10. (*a*) Write the equation for the reaction between sodium hydroxide and hydrochloric acid, representing all the ions present. (*b*) Why does the reaction go to completion?

THOUGHT QUESTIONS

1. In preparing carbon dioxide by the action of hydrochloric acid on marble the reaction goes to completion without heating. In preparing nitric acid by the action of sulfuric acid on sodium nitrate (p. 296) it is necessary to heat the mixture. Why is heat necessary in the one case and not in the other?

2. If the substances represented below react, complete and balance the equation. If the reaction is reversible, indicate this fact in the usual way. Indicate in the usual way the gases and insoluble products formed. (See Table of Solubilities in Appendix D and Electromotive Series on page 261 for certain data needed.)

(*a*) $Zn + H_2SO_4$
(*b*) $NaNO_3 + H_2SO_4$
(*c*) $AgNO_3 + KCl$
(*d*) $HCl + Ag$
(*e*) $NaOH + HNO_3$
(*f*) $BaCl_2 + H_2SO_4$
(*g*) $Ca(OH)_2 + CO_2$
(*h*) $Na_2CO_3 + HCl$
(*i*) $HCl + H_2O$
(*j*) $ZnCl_2 + Cu$
(*k*) $AgNO_3 + Cu$
(*l*) $Na_2SO_4 + Zn$
(*m*) $NaNO_3 + KCl$
(*n*) $H_2SO_4 + H_2O$
(*o*) $NaOH + NH_4Cl$
(*p*) $KNO_3 + Cu$

OPTIONAL EXERCISES

1. One of the preparations used for destroying germs of fungus diseases on trees is made by adding a solution of copper sulfate ($CuSO_4$) to calcium hydroxide ($Ca(OH)_2$) in a tank of water. (*a*) Is there any objection to dissolving the copper sulfate in an iron kettle? (*b*) Write an equation representing the equilibrium between the copper sulfate and its ions when dissolved in water. (*c*) Do you think any reaction will take place between the copper sulfate and calcium hydroxide? Give your reasons.

2. Suggest conditions for making the reaction represented below go in either direction:

$$NH_3 + H_2O \rightleftarrows NH_4OH$$

3. Barium sulfate ($BaSO_4$) is a white insoluble compound used in paints. Suppose you had a supply of barium chloride ($BaCl_2$) and wished to convert it into barium sulfate. (*a*) Suggest one or more methods for doing this, and explain the reactions. (*b*) Try out your suggestions in the laboratory.

UNIT READINGS

BERRY. *Stuff*. [Chapter II, "A Breath of Fresh Air," tells about the gases in the air. Chapter VIII, "Cold Stuff," tells about the manufacture of ice.]

CADY. *Journal of Chemical Education*, Vol. VIII, pp. 1027–1043. [An interesting and well-illustrated article on liquid air.]

CLARKE. *Marvels of Modern Chemistry*. [Chapter XI gives interesting facts about nitrogen.]

FOSTER. *The Romance of Chemistry*. [Read about nitrogen, pp. 188–197.]

HARROW. *Eminent Chemists of Our Times*. [Pages 41–58 give a very interesting account of Ramsay and his discovery of the inert gases.]

HOLMES. *Out of the Test Tube*. [Read Chapter XIV, "The Romance of the Lazy Elements."]

PHELPS. *Chemistry in Medicine*. [Chapter III, Article 2, is entitled "The Need of Air: Good and Bad Air."]

SADTLER. *Chemistry of Familiar Things*. [Chapter VI, "Air, Oxidation, and Ventilation," is simple and interesting.]

SLOSSON. *Creative Chemistry*. [Students will enjoy reading Chapter II, "Nitrogen — Preserver and Destroyer of Life."]

WEEKS. *The Discovery of the Elements*. [The discovery of nitrogen, pp. 33–35; of the inert gases, pp. 278–289. Of great interest.]

The Science Leaflet. [No. 7 of recent volumes tells of nitrogen; No. 8, of air. Interesting and important.]

The World Book Encyclopedia. [Contains a good article, well illustrated, about ice.]

Unit Seven. A Group Picture of the Chemical Family

WE HAVE learned that ninety-two elements make up the material part of our universe. On first acquaintance these elements seem to be a mixed lot, with little relation to each other. Some are gases, some liquids, others solids; some are inert, others very active; some are essential to life, others are poisonous.

Many years ago the great Russian chemist Mendeléeff showed that these ninety-two elements are not unrelated but form one large family, the members of which, arranged in tabular form, show a regular gradation in properties. That this table brings to light real relationships between the elements is proved by the fact that it enabled Mendeléeff to predict the discovery of a number of elements, as well as their properties. It was not long before many of these predictions were verified.

Further studies have shown that the large family of elements is made up of a number of smaller families whose members are still more intimately related.

In this unit we shall draw a picture of the large chemical family and of its division into natural groups. To illustrate how the members of these smaller groups are related to each other we shall study one typical group, named, from its best-known member, the chlorine family.

CHAPTER XXVIII

The Periodic Law

I. FAMILY GROUPS OF SIMILAR ELEMENTS

Introduction. The practical gardener must know a little about a great many varieties of plants. Instead of trying to learn all about each variety separately, he saves time and effort by putting them into groups purely for convenience. One group will grow best in abundant sunshine, another in shady places; one group needs plenty of water, another will stand dry weather well; one flourishes best in a clay soil, another requires a sandy loam. This is merely a *practical* classification and is not based on any important property of the plants. It brings together many different kinds in the same group.

The scientific botanist feels that there must be a much more fundamental basis for classification. He thinks of plants as *related* to each other, — as brothers and sisters, as cousins, as distant relatives, — and he tries to trace out these relationships. He wants to find a *natural* classification.

Classification of the elements. The earlier chemists classified the elements much as a gardener classifies plants, having in mind only convenience and practical use. They grouped them as metals and nonmetals; as heavy elements, light elements, and gaseous elements; as acid-forming elements and base-forming elements.

As the number of known elements increased and more was learned about them, chemists were convinced that some sort of *natural* relation exists between elements just as between plants. They felt sure that if this relationship could be discovered, and the elements were arranged in *natural* groups or families, the study of chemistry would be much easier and the discovery of many new facts would result.

Many ingenious and interesting plans for classifying the elements were proposed from time to time, and finally, in 1869, the Russian chemist Mendeléeff (Fig. 225) discovered a natural relationship known as the *periodic law.* This was based upon the *atomic weights* of the elements. Since about 1914 it has rested upon the *atomic numbers* of the elements.

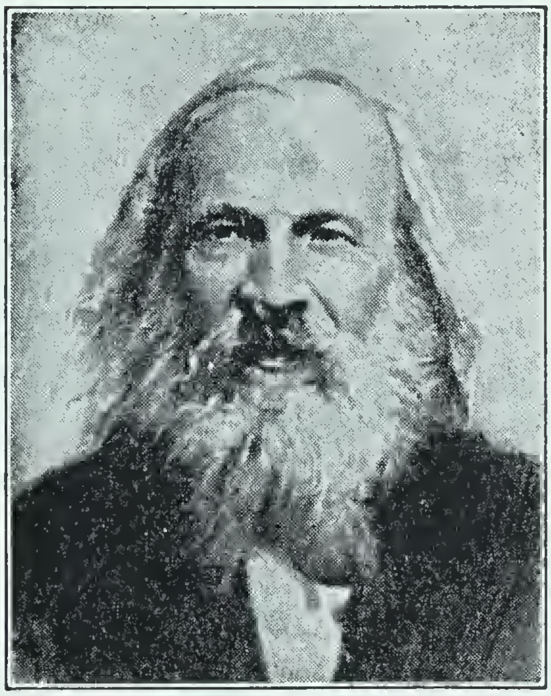


FIG. 225. D. I. Mendeléeff (1834–1907)

A Russian chemist who is noted chiefly for proposing the periodic classification of the elements

FIG. 226. H. G. J. Moseley (1888–1915)

The English physicist who proved that the properties of an atom depend upon its atomic number

The atomic numbers of the elements can be directly determined. It will be recalled (p. 172) that the nuclear charge of an atom of an element is equal to the number of protons in its nucleus, and that this nuclear charge is known as the *atomic number* of the element. In 1913–1914 the young English physicist Moseley (Fig. 226), killed early in the World War, hit upon a remarkable method for measuring *directly* the nuclear charge of each of the various kinds of atoms. Moseley's method was a purely physical one, somewhat complicated, and need not be described here. It is of importance to remember merely that each element has its atomic number and that this can be found out *by experiment.*

From the results of his experiments, Moseley arranged the elements in a row in the order of their atomic numbers. Hydrogen is number 1 (atomic number 1), helium is number 2 (atomic number 2), lithium is number 3 (atomic number 3), and so on up to uranium, whose atomic number is 92.

The periodic grouping. Now we can arrange the elements *in the order of their atomic numbers* in a way that brings to light most interesting relationships. For a reason to be explained later, we will omit hydrogen, which has the smallest atomic number (1). Beginning with helium, of atomic number 2, the succeeding seven elements are arranged in a horizontal row *in the order of their atomic numbers*, as in the first line of the table below. These eight elements differ markedly from each other in chemical behavior, but neon, of atomic number 10, is very similar to helium. It is placed just below helium, and a new horizontal row follows, as shown in the table. The element following chlorine, namely argon, resembles helium and neon and begins a third row.

TABLE OF TWENTY-FOUR ELEMENTS

He (2)	Li (3)	Be (4)	B (5)	C (6)	N (7)	O (8)	F (9)
Ne (10)	Na (11)	Mg (12)	Al (13)	Si (14)	P (15)	S (16)	Cl (17)
A (18)	K (19)	Ca (20)	Sc (21)	Ti (22)	V (23)	Cr (24)	Mn (25)

Now if we notice the elements that fall in *vertical* columns in these three rows, a remarkable fact comes to light. Not only is there a strong similarity between helium, neon, and argon, which form the first vertical column, but *the elements in each of the other columns have the same kind of similarity among themselves and evidently form natural groups.* Lithium, sodium, and potassium form a group of similar elements, as do also beryllium, magnesium, and calcium.

Now, just as we have arranged the elements of low atomic numbers, in the three rows given above, we may keep on in this general way to include all the elements in a single table. This table is given on page 323. It will be noted that the elements making up each horizontal row are called a *period*, while those in vertical columns are called *groups.* Hydrogen by itself constitutes one period. Then follow the three periods given in the table above.

Following manganese in the order of their atomic numbers come three elements, iron, cobalt, and nickel. These three elements have atomic weights much nearer together than do any of the elements of smaller atomic numbers. They resemble each other strongly, but are not like any of the elements so far considered. So we place the three together in a new group, namely, Group VIII.

The Periodic Arrangement of the Elements according to Atomic Numbers

Type of hydride		RH	RH_2	RH_3	RH_4	RH_3	RH_2	RH			
Type of oxide		R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4		
PERIOD	GROUP 0	GROUP I	GROUP II	GROUP III	GROUP IV	GROUP V	GROUP VI	GROUP VII	GROUP VIII		
0		1 H = 1.008									
1	2 He = 4.003	3 Li = 6.94	4 Be = 9.02	5 B = 10.82	6 C = 12.01	7 N = 14.008	8 O = 16.000	9 F = 19.00			
2	10 Ne = 20.183	11 Na = 22.997	12 Mg = 24.32	13 Al = 26.97	14 Si = 28.06	15 P = 30.98	16 S = 32.06	17 Cl = 35.457			
3		*A* *B*	*A* *B*	*A* *B*	*A* *B*	*A* *B*	*A* *B*	*A* *B*			
	18 A = 39.944	19 K = 39.096	20 Ca = 40.08	21 Sc = 45.10	22 Ti = 47.90	23 V = 50.95	24 Cr = 52.01	25 Mn = 54.93	26 Fe = 55.85	27 Co = 58.94	28 Ni = 58.69
		29 Cu = 63.57	30 Zn = 65.38	31 Ga = 69.72	32 Ge = 72.60	33 As = 74.91	34 Se = 78.96	35 Br = 79.916			
4	36 Kr = 83.7	37 Rb = 85.48	38 Sr = 87.63	39 Y = 88.92	40 Zr = 91.22	41 Cb = 92.91	42 Mo = 95.95	43 Ma = ?	44 Ru = 101.7	45 Rh = 102.91	46 Pd = 106.7
		47 Ag = 107.88	48 Cd = 112.41	49 In = 114.76	50 Sn = 118.70	51 Sb = 121.76	52 Te = 127.61	53 I = 126.92			
5	54 Xe = 131.3	55 Cs = 132.91	56 Ba = 137.36	57–71 * Rare Earths	72 Hf = 178.6	73 Ta = 180.88	74 W = 183.92	75 Re = 186.31	76 Os = 190.2	77 Ir = 193.1	78 Pt = 195.23
		79 Au = 197.2	80 Hg = 200.61	81 Tl = 204.39	82 Pb = 207.21	83 Bi = 209.00	84 Po = 210(?)	85 ?(†)			
6	86 Rn = 222	87 ?(†)	88 Ra = 226.05	89 Ac = ?	90 Th = 232.12	91 Pa = 231	92 U = 238.07				

* The atomic numbers are printed in red, and the atomic weights in black. In Group III, upper row of Period 5, we find a number of elements of atomic numbers 57 to 71 inclusive. These are known as the *rare-earth elements*. They closely resemble each other in properties and do not fit well into a simple table.

† The discovery of elements of atomic numbers 85 and 87 is claimed but lacks confirmation.

Following nickel, of atomic number 28, comes copper (atomic number 29). This element evidently does not belong with helium, neon, and argon in Group 0; for it has none of the properties of these elements. In some ways it does resemble the elements in Group I; so we place it there. Then follow in regular order of atomic numbers the elements as far as bromine. After bromine comes krypton, which closely resembles the other elements in Group 0, where we have placed it; and we follow it with the elements as far as masurium (atomic number 43). After masurium comes another group of three elements whose atomic weights lie close together; so we place them in Group VIII. In the same general way the remaining elements are fitted into the table. The complete arrangement of the elements is called *the periodic arrangement of the elements according to atomic numbers.*

The rare-earth elements. If we study the table carefully, we will notice that in Group III, upper row of Period 5, there are brought together a number of elements of atomic numbers 57 to 71 inclusive. These elements are called the *rare-earth* elements. In all chemical ways they resemble each other very closely. Most of them really are very rare and as yet have few uses. They can be fitted into the table, but this adds some complications. It is best to omit them in an elementary textbook.

The properties of the elements and their atomic numbers. When we compare the elements in Period 1 with each other, we find that their properties change in an interesting way as the atomic number increases. Helium combines with no other element. Following it, lithium is a metallic element, has a valence of 1, and is strongly base-forming. The next element, beryllium, has a valence of 2, and is less strongly base-forming. Boron, with a valence of 3, has few base-forming and many acid-forming properties. In carbon, with a valence of 4, all base-forming properties have disappeared, and the acid-forming properties are more marked than in boron. These become still stronger as we pass through nitrogen and oxygen, and on reaching fluorine we have one of the strongest acid-forming elements. *The properties of* *these eight elements vary more or less regularly with their atomic numbers*; or, in mathematical language, *their properties are regular functions of their atomic numbers.*

Properties of elements repeated. If it were true that helium had the smallest atomic number of all the elements and fluorine the largest, so that in passing from one to the other we should include all the elements, we could say that the properties of *all* the elements are *regular* functions of their atomic numbers.

But fluorine is an element of relatively small atomic number, and the one following it, neon, breaks the order; *for in it reappear all the characteristic properties of helium.* Sodium, following neon, bears much the same relation to lithium that neon does to helium; and in general the properties of the elements in Period 2 vary in the same way as do the properties of the elements in Period 1 until argon is reached. Then another repetition begins, argon being similar to helium and neon.

The periodic law. We see, then, that the properties of the elements do not vary in a *steady progression* with the atomic number, but at regular intervals there is a *repetition*, or, as mathematicians say, a *period.* This is called the *periodic law.*

The periodic law: The properties of elements are periodic functions of their atomic numbers.

Two families in a group. After Period 2 (p. 323) the elements of each group (excepting Group 0) fall naturally into two subdivisions called *families.* Each *period* after the second consists of two rows across the table. The elements in the *first* row in any group form one family; those in the *second* row, the other. In the table these families are arranged under the headings *A* and *B*. The elements in family *A* in a group resemble one another much more closely than they resemble those in family *B* of the same group. For example, zinc, cadmium, and mercury form one family of very similar elements in Group II, while calcium, strontium, barium, and radium form the other.

The first two elements in each group (omitting hydrogen, in Group I) resemble one of the families (*A* or *B*) much more closely than the other. In Group I lithium and sodium resemble potassium, rubidium, and cesium rather than copper, silver, and gold. In Group VII fluorine and chlorine resemble bromine and iodine rather than manganese and the other elements in family *A*, and the positions assigned them in the table indicate this fact.

Family resemblances. What do we mean by saying that the elements that make up a family resemble each other?

1. ***Valence.*** In general the elements in a family have the same valence (or valences). This means that the elements in a family have the same number of valence electrons (p. 205). So the formulas of many of their compounds are similar. The formulas R_2O, RO, etc., placed above the group columns in the table, represent the usual oxides of the elements in each column, while the formulas RH, RH_2, etc. represent the hydrides or chlorides. In either case the letter R stands for the symbol of any one of the elements in either family.

2. ***Chemical conduct.*** The members of a family resemble each other in their chemical action. If one is a metal, the others usually are; if one is a nonmetal, so, too, are the others. There is also a somewhat regular gradation in the conduct of the elements *in each family.* If the top element is strongly acid-forming, as is nitrogen (Group V), the succeeding ones are less so; and the lowest one may even have metallic properties, as is true of bismuth. The elements between the top and the bottom are intermediate in their chemical nature.

3. ***Physical properties.*** In the same way the physical properties of the members of a family are in general somewhat similar, and show a regular gradation as we pass from element to element in the family. The melting point, boiling point, density, and electrical conductance usually vary more or less regularly from element to element.

Value of the periodic law. The periodic law has been of great service in the development of the science of chemistry.

1. ***It simplifies study.*** It is easy to see that the regularities brought to light among the elements simplify the study of chemistry. A thorough study of one element of a family makes a study of the others a much easier task.

2. ***It indicates probable error.*** When the periodic law was first announced, the physical constants of many of the elements, as then measured, did not agree with those required by the law. For example, many atomic weights were wrong. A further study of most of these cases showed that errors of measurement had been made, and these were speedily corrected.

3. ***It suggests the probable existence of new elements.*** When the periodic law was first announced, there were a number of vacant places in the table which evidently belonged to elements not yet discovered. From their position in the table it was possible to predict the properties of these missing elements, and even the kinds of ores in which they would probably be found. As these elements were discovered their properties were found to agree in a remarkable way with those predicted for them.

The atomic numbers of the elements range from 1 to 92, and, of the ninety-two elements predicted, all are known with some certainty except numbers 85 and 87. The discovery of these two elements has been announced but lacks confirmation.

The periodic law is not perfect. Like most scientific laws, the periodic law has its imperfections and limitations, which shows that we have not yet got all the facts.

Hydrogen has but one electron, whereas all the other elements have two electrons in their innermost orbit, close to the nucleus. This difference may account for the fact that hydrogen forms a period by itself.

The similarities between elements in a family are *merely general*, not exact. We are never *certain* that an element will behave as its position predicts until we try it out. It usually acts at least approximately as we should expect it to act.

II. ISOTOPES, ATOMS OF THE SAME ELEMENT BUT WITH DIFFERENT WEIGHTS

Our idea of the atom has changed. Until recent years everyone thought that all the atoms of any given element have exactly the same weight. The discovery that many of the elements are made up of atoms of two or more different weights was unexpected and has made us change many of our old ideas. The student will ask, "If two atoms are of different weights, must they not be atoms of different elements?" To answer this question we must start by recalling some things we have already learned.

Fig. 227. Sir J. J. Thomson (1856–1940)

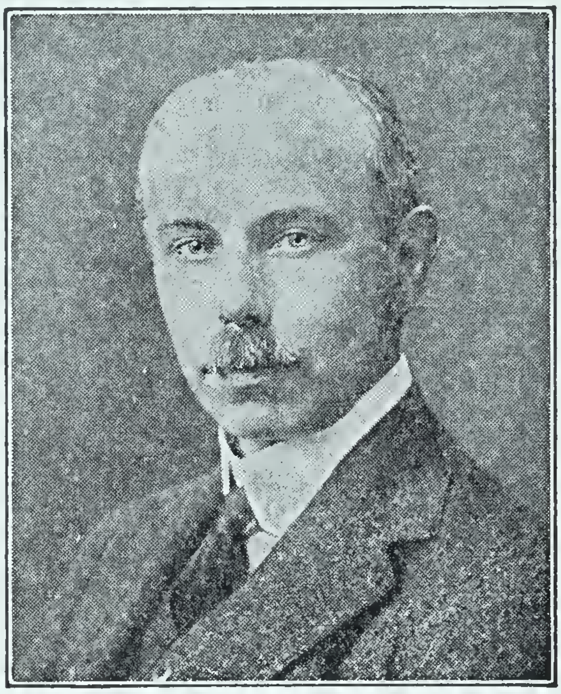


Fig. 228. F. W. Aston (1877–   )

Two English physicists who proved that many of the elements are mixtures of isotopes

We have found (1) that the *weight* of an atom depends almost entirely on the weight of the protons and neutrons in its nucleus and (2) that the *chemical conduct* of an atom depends on its valence electrons. In this chapter we have learned (3) that the position of an element in the periodic table depends on its nuclear charge (atomic number).

A possible solution. Now if we could have two atoms with the same nuclear charge (protons) and the same number of valence electrons, *but with different nuclear weights* (different number of neutrons), we should have two atoms of the same chemical properties and therefore indistinguishable from each other chemically, but with different weights. In other words, we should have two atoms of the *same element* with different atomic weights.

Isotopes. Two brilliant physicists, J. J. Thomson (Fig. 227) and F. W. Aston (Fig. 228), have proved that many elements do actually have atoms of several different weights. Fig. 229 represents the two different atoms of lithium. Each has a nuclear charge of 3 (+), and each has 1 valence electron. They are therefore atoms of the same element. But one has a weight of 6 (3 protons and 3 neutrons), while the other has a weight of 7 (3 protons and 4 neutrons). Chemically they are just alike.

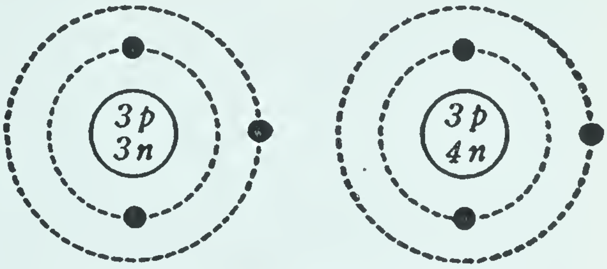


Fig. 229. The isotopes of lithium

Atoms of the same element, with the same nuclear charge but with different weights, are called isotopes of that element.

In the nucleus of all the isotopes of an element the number of *protons* is the same. It is the neutrons that vary in number, giving atoms of different weights.

A FEW EXAMPLES OF ISOTOPES

ELEMENT	ATOMIC NUMBER	ATOMIC WEIGHT	ISOTOPIC WEIGHTS IN ORDER OF ABUNDANCE
Hydrogen	1	1.0081	1, 2
Lithium	3	6.94	7, 6
Oxygen	8	16.000	16, 18, 17
Neon	10	20.183	20, 22, 21
Magnesium	12	24.32	24, 25, 26
Chlorine	17	35.457	35, 37
Argon	18	39.944	40, 36, 38
Potassium	19	39.096	39, 41, 40
Zinc	30	65.38	64, 66, 68, 67, 70

Fractional atomic weights. Since the weight of an atom is really the weight of its nucleus, and since the nucleus is always made up of a definite number of protons and neutrons (all of equal weight), *the weights of all atoms should be whole numbers* (p. 184). Yet many elements have fractional atomic weights. For example, chlorine has the atomic weight 35.457. The reason for this is now clear. All elements that have fractional atomic weights have been shown to be mixtures of two or more isotopes, and each individual isotope has an atomic weight that is a whole number. The *fractional* atomic weight of an element is merely the average of the weights of the mixture of its isotopes. Generally one of the isotopes is present in much the larger percentage. For example, hydrogen has three isotopes, of atomic weights 1, 2, and 3. In hydrogen, as ordinarily prepared, the isotope of atomic weight 2 is present to the extent of only 1 part in 6000, while that of atomic weight 3 is present in much smaller amounts — 1 part in several millions. Tin has as many as eleven distinct isotopes.

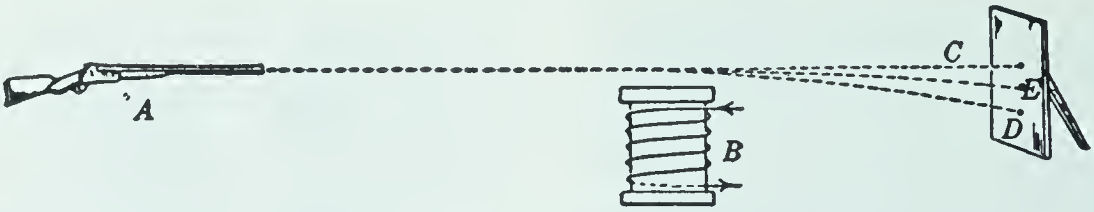
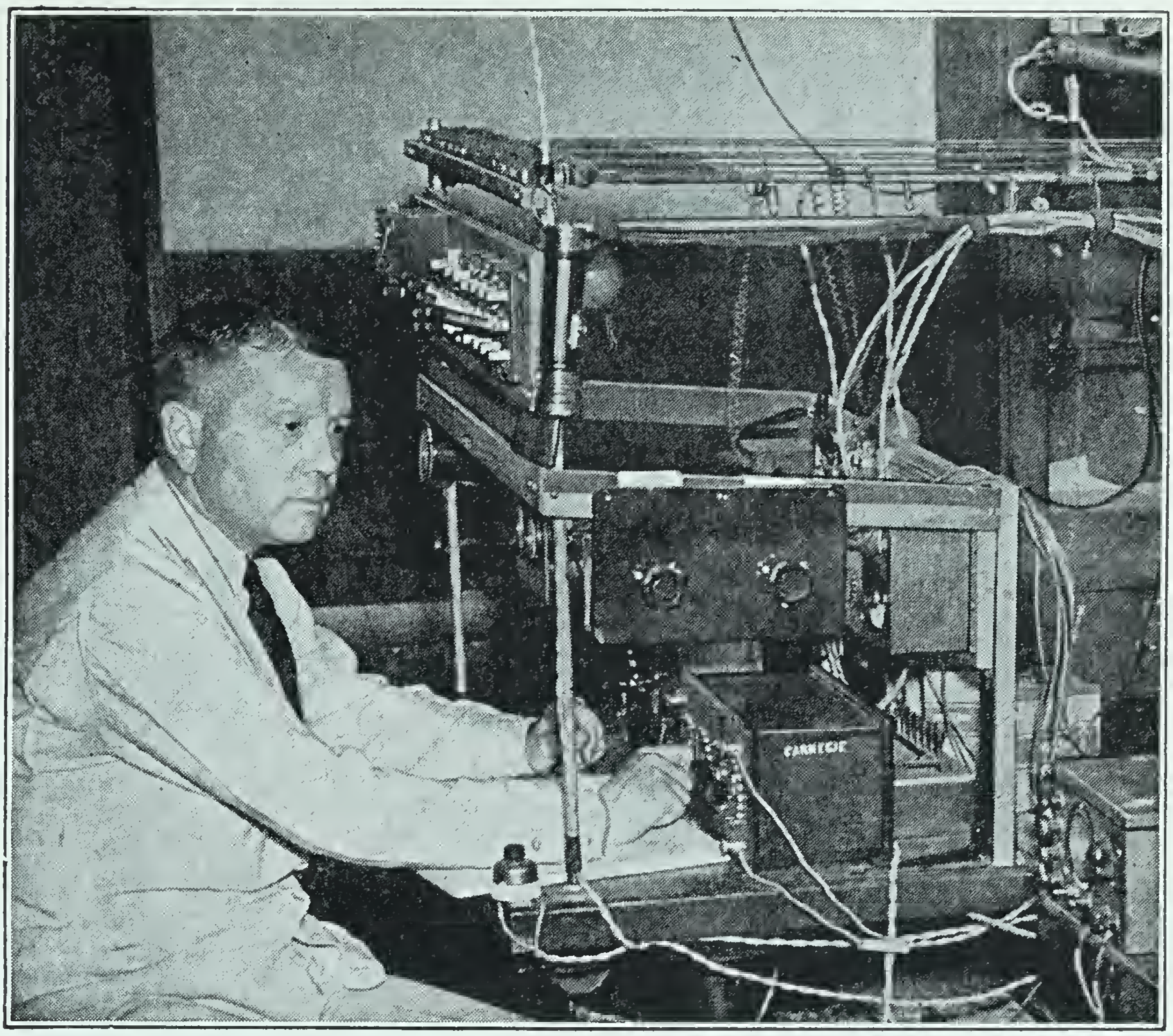


FIG. 230. Illustration of Thomson's method of proving the existence of isotopes

How Thomson proved that the atoms of some elements differ in weight. In his efforts to find out whether or not all the atoms of an element have the same weight, Thomson (p. 328) first experimented with the element neon. The method he used can be illustrated in the following way:

Everyone knows that a magnet attracts iron. Now if we should shoot iron bullets of two different weights from the gun *A* (Fig. 230) to the target *C*, their path lying close to the powerful magnet *B*, the lighter bullets in passing the magnet *B* would be pulled more out of their straight-line course than would the heavier ones. They would strike the target *C* at a point *D*, whereas the less deflected, heavier bullets would strike at *E*. If we could make all the necessary measurements, we could calculate the weights of the two kinds of bullets from the two deflections *D* and *E*.

Instead of bullets, Thomson shot charged ions of neon past a powerful magnet in such a way that they hit a photographic plate as a target. Now if the neon ions were all of the same weight, they would all be deflected to the same extent. Thomson found on developing the plate that one group of ions were deflected to the same extent, and that a second group showed a greater deflection. The deflections of the two varieties of ions from a straight line were then measured, and the weights of the ions calculated. In this way Thomson found that there were two varieties of neon atoms,



Wide World

Fig. 231. Harold C. Urey in his laboratory at Columbia University

He was awarded the Nobel prize in 1934 for his discovery of the isotope of hydrogen of atomic weight 2

one with atomic weight 20, and the other with weight 22. He found, moreover, that in ordinary neon, for every atom of mass 22, there are nine neon atoms of mass 20. The isotope of weight 21 was discovered later and is much less abundant.

There are 92 elements, but there are several hundred known *varieties of atoms.*

The isotopes of hydrogen; heavy water. In 1934 Professor Harold C. Urey (Fig. 231) and those working with him discovered an isotope of *hydrogen* of atomic weight 2, and a little later the discovery of a third isotope, of atomic weight 3, was announced, but there is doubt of its existence. To distinguish these from hydrogen of atomic weight 1, the isotope of atomic weight 2 is called *deuterium*, while that of atomic weight 3 was called *tritium.*

Chemists had long thought that each molecule of water was made up of two atoms of hydrogen of atomic weight 1 combined with one atom of oxygen of atomic weight 16. After the discovery of the isotopes of hydrogen, chemists sought to obtain a water in which the hydrogen atoms present should each have an atomic weight of 2. This compound has now been obtained in a pure state, and is called *deuterium oxide* or *heavy water.* Its molecular weight is $2 + 2 + 16$, or 20, while that of water containing hydrogen of atomic weight 1 is $1 + 1 + 16$, or 18.

Experiments show that there is about 1 part of heavy water in 6000 parts of ordinary water. When ordinary water is electrolyzed, the lighter product (molecular weight 18) is decomposed more readily than the heavier product (molecular weight 20). By repeating the process many times the pure heavy water can be obtained.

Heavy water has all the appearance of ordinary water, but differs from it in many of its properties. It freezes at 3.8°, boils at 101.42°, and its maximum density is at 11.6°. Animals and plants do not thrive on it as on ordinary water, although it is not especially poisonous.

CHAPTER SUMMARY IN QUESTION FORM

1. What is the advantage of classifying elements and compounds into groups or families?

2. (*a*) Who discovered that a natural relationship exists between the properties of elements and their atomic weights? (*b*) What name was given to the law that expresses this relationship?

3. In what way has the periodic law been improved in more recent years?

4. (*a*) Explain clearly what is meant by the term *atomic number.* (*b*) Who discovered a method for directly measuring the atomic number of an element?

5. State how the elements are arranged in the table on page 323.

6. (*a*) State the periodic law. (*b*) What is meant by the term *periodic function* in the statement of the law?

7. Show how each group of elements is divided into "families" of elements.

8. State three ways in which the elements constituting a family resemble each other.

9. State three ways in which the periodic law has been of great service in the development of the science of chemistry.

10. What imperfections remain in the law as stated at present?

11. (*a*) Who first proved that it is possible for atoms of the same element to have different atomic weights? (*b*) Illustrate how this can be so, using neon as an example.

12. What do we mean when we say that oxygen has three isotopes?

13. (*a*) How many isotopes has hydrogen? (*b*) What are the relative amounts of each of these isotopes in hydrogen as ordinarily prepared?

14. (*a*) How does "heavy water" differ in composition from ordinary water? (*b*) Contrast the properties of the two.

THOUGHT QUESTIONS

1. Do the isotopes of an element differ (*a*) in atomic numbers? (*b*) in the number of protons present in each atom? (*c*) in the number of neutrons present? (*d*) in the number of electrons?

2. Explain why some elements have fractional atomic weights and others do not.

3. By examining the periodic table it will be seen that the atomic weights of a few of the elements have never been determined. (*a*) Could you approximate the atomic weights of these elements from their position in the table? (*b*) Could you make a good guess as to some of their properties?

4. Would the arrangement of the elements in the periodic table according to their atomic weights have to be identical with the arrangement according to their atomic numbers?

OPTIONAL EXERCISES

1. Write a theme on the subject "Atomic Numbers" which will include the following topics: (*a*) meaning of the term; (*b*) diagrams of the atoms of a number of elements, showing the atomic number of each; (*c*) how the atomic number serves as a natural classification of the elements; (*d*) how this classification has been of great service to the chemist.

2. Oxygen as well as hydrogen has three isotopes (see table, p. 329). Calculate the number of different possible compounds made up of two atoms of hydrogen and one of oxygen.

CHAPTER XXIX

The Chlorine Family

[A Family of Four Very Similar Elements]

Name	Atomic Weight	Electrons in Each Orbit	Melting Point	Color and State
Fluorine (F) .	19.00	2 : 7	– 223°	Pale-yellowish gas
Chlorine (Cl) .	35.457	2 : 8 : 7	– 101.6°	Greenish-yellow gas
Bromine (Br) .	79.916	2 . 8 : 18 : 7	– 7.2°	Red liquid
Iodine (I) . . .	126.92	2 : 8 : 18 : 18 : 7	113.5°	Purplish-black solid

The periodic family. These four elements are a good example of a periodic family. They have general family resemblances, but many personal traits, just as in a family of four children. As can be seen in the table, the four elements show a general change, or gradation, in properties as we pass from one to the other, while the children in a family are usually not so easy to arrange in a graded order.

These elements are often called the *halogens*, a word meaning "producers of salt," because nearly all their compounds are soluble and so tend to accumulate in sea water and in salt beds. Chlorine and its important compound hydrogen chloride have already been studied in Chapter XIX, and the student should review that chapter at this time.

FLUORINE

Fluorine — what it is like and why it is rarely seen. It is safe to say that the student of this text has never seen fluorine. Few people have. This is because the element has been difficult to prepare and by itself has no uses. Though known for a long time, it has been somewhat of a forgotten element; but a number of its compounds are rapidly becoming important.

Fluorine is a pale-yellowish gas, difficult to liquefy and freeze. When set free in the presence of water (nascent state), it decomposes the water, forming hydrogen fluoride (HF), oxygen, and an oxide of fluorine. In general it will take away hydrogen from almost any compound.

The mineral fluorite (CaF_2). Fluorite, also called fluorspar (Fig. 232), is the most important natural compound of fluorine, and from this all the other compounds of the element are made. The complex mineral called *apatite* (see phosphates) is its most abundant mineral. *Cryolite*, Na_3AlF_6, is a mineral that made possible the production of aluminum on a large scale. Apparently we must have traces of fluorides for our bones and especially for our teeth. But more than a trace in our drinking water results in "mottled teeth," and some cities have had to seek a new water supply because of too much fluorine in the old one.

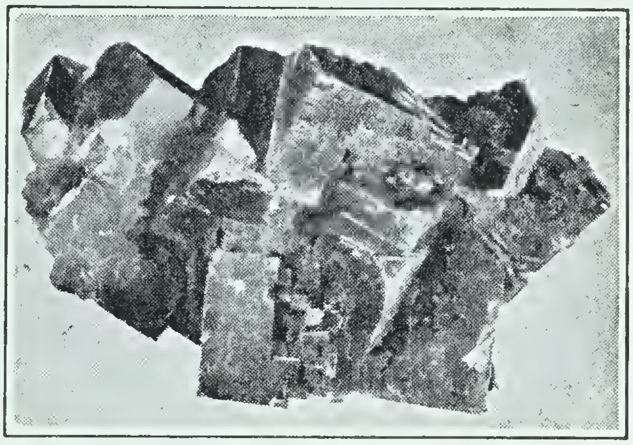


Fig. 232. A cluster of crystals of the mineral fluorite (CaF_2)

Preparation. It is not very difficult to set fluorine free from fluorides, but the trouble is that the nascent fluorine at once attacks almost anything that may be present. In 1886 the French chemist Moissan (Fig. 233) finally succeeded in obtaining it in a free state in platinum vessels. It is now usually prepared by the electrolysis of melted potassium hydrogen fluoride (KHF_2) in copper vessels. When the *molecular* gas has formed, it is not so active as was formerly believed.

Hydrogen fluoride (HF); hydrofluoric acid. Hydrogen fluoride is a liquid of low boiling point (19.4°). It is made by the action of sulfuric acid on the mineral fluorite (CaF_2):

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2\ HF\uparrow$$

It is soluble in water in all proportions, forming *hydrofluoric acid.* This is not as strong an acid as is hydrochloric acid, but it has a very destructive action on skin and flesh and must be handled with great care. It is kept in bottles made of wax (ceresin) (Fig. 234), because it acts on glass.

Action on silica and glass. Hydrofluoric acid is the only acid that acts readily on silica (SiO_2) and its compounds, which include sand, quartz, glass, and many minerals. Its

A
HENRI·MOISSAN
MEMBRE DE L'INSTITUT
EN·SOUVENIR
DU 20ME ANNIVERSAIRE
DE·SA·DECOUVERTE
DU·FLUOR
SES·ELEVES
SES AMIS
1886 1906
HENRI MOISSAN

Fig. 233. A tablet erected by the associates and friends of Moissan in his laboratory in Paris, in 1906, on the twentieth anniversary of the isolation of fluorine

practical uses depend upon this fact. In the reaction on these materials the element silicon is converted into silicon fluoride (SiF_4), which is a gas:

$$SiO_2 + 4\ HF \longrightarrow SiF_4\uparrow + 2\ H_2O$$

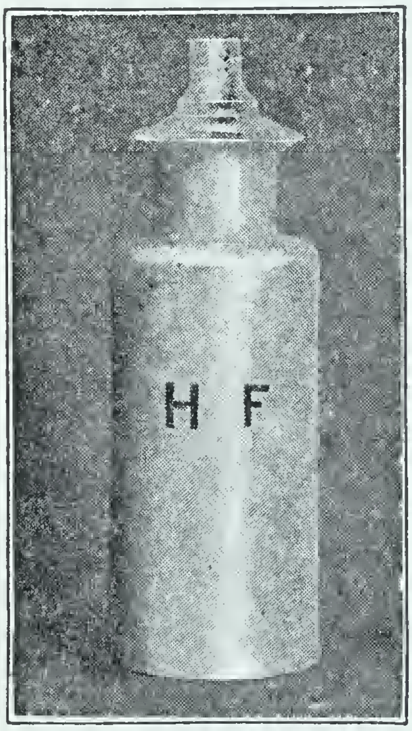
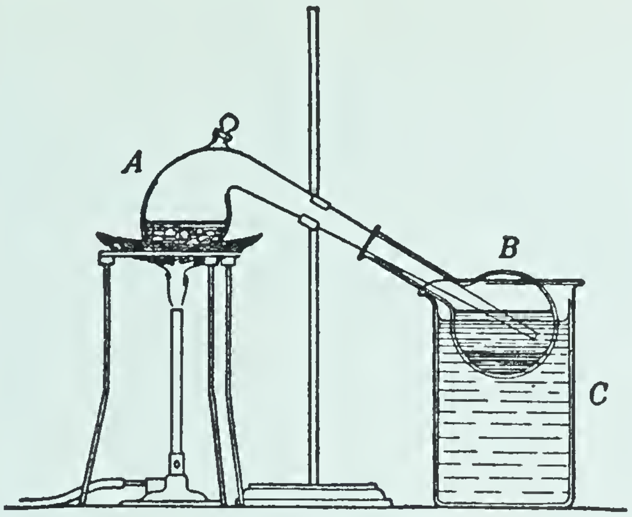


Fig. 234. A wax bottle for hydrofluoric acid

The chief use for hydrofluoric acid is in chemical analysis and in etching (frosting) glass. Practically all the electric-light bulbs now made are frosted. They are etched on the *inside* by filling the bulb for a short time with hydrofluoric acid. Etching a design on glass is done by covering the glass with wax, scratching the design through the wax, and then exposing the prepared surface to fumes of gaseous hydrogen fluoride or wetting it with hydrofluoric acid. The wax is then removed, leaving the design etched on the glass.

Ammonium fluoride, NH_4F, has a large use as an insecticide. A compound of the formula CCl_2F_2 is a low-boiling liquid widely used in mechanical refrigerators (p. 60).



A mixture of manganese dioxide, sodium bromide, and sulfuric acid is placed in the retort *A*, the end of which just touches the water in the flask *B*, which is partly immersed in ice water in beaker *C*. As the contents of the retort are heated, the bromine is set free, distills over, and collects under the water in flask *B*

FIG. 235. The preparation of bromine in the laboratory

BROMINE

What bromine is like. This element, discovered by the French chemist Balard in 1826, is a heavy, dark-red liquid which boils at 58.7° and freezes at − 7.2°. It vaporizes readily at ordinary temperatures. This vapor has an unpleasant odor and is very irritating to the eyes and throat. One volume of the liquid dissolves in about 100 volumes of water, and it is readily soluble in carbon tetrachloride and similar solvents. It resembles chlorine in its chemical conduct, except that it is less active.

Where bromine is found. All salt waters contain a small percentage of the ion Br^-. When these waters are evaporated, the bromine is deposited as a salt of bromine and a metal (generally calcium or magnesium). These salts are called *bromides*. The salt waters of Michigan and the Ohio River valley are the richest in bromides and have long been the chief source of the bromine of commerce. At present more than half of the bromine produced in the United States is obtained from sea water.

How we get bromine. The methods used for preparing chlorine in the laboratory (p. 219) are just as good for getting bromine (Fig. 235). But instead of hydrobromic acid (HBr) we use a mixture of sodium bromide and sulfuric acid:

$$MnO_2 + 2\ NaBr + 2\ H_2SO_4 \longrightarrow Na_2SO_4 + MnSO_4 + 2\ H_2O + Br_2\uparrow$$

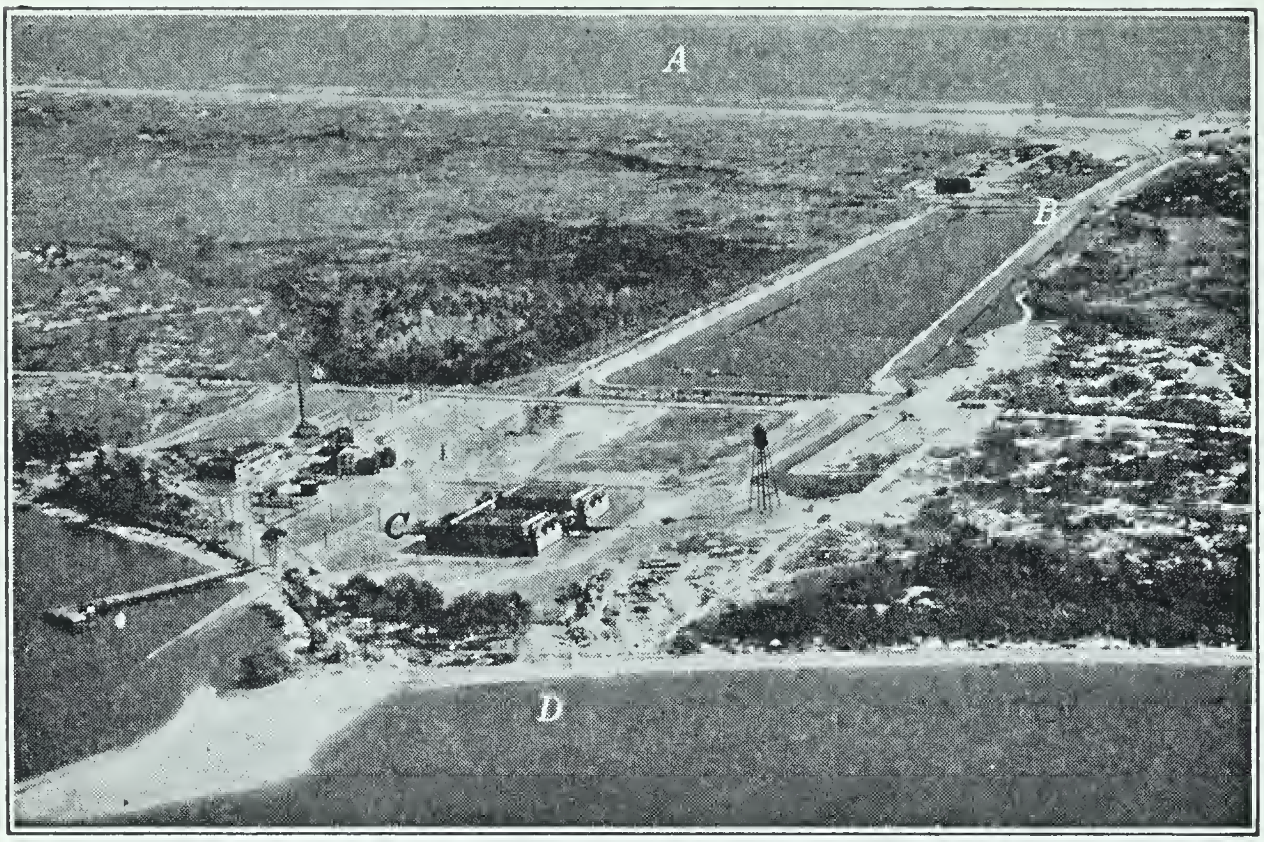


Fig. 236. A plant, constructed on the shore of the Atlantic Ocean in North Carolina, for obtaining bromine from sea water

The water, containing about 1 pound of bromine in 2000 gallons, is led from the shore of the Atlantic Ocean (*A*) through a canal (*B*) to the plant (*C*), equipped with apparatus for the removal of the bromine. After the bromine has been removed, the water flows on into the Cape Fear River (*D*). (Aerial Explorations, Inc., courtesy of Ethyl-Dow Chemical Co.)

Commercially bromine is prepared chiefly by passing an electric current through salt waters containing dissolved bromides. Bromine and some chlorine are set free, and the chlorine then acts upon any unchanged bromides, setting free bromine:

$$2\,NaBr + Cl_2 \longrightarrow 2\,NaCl + Br_2\uparrow$$

A great deal of bromine from very little. When there is a sharp industrial demand for a chemical material, it can usually be produced. Bromine had a great boom when certain compounds prepared by the use of the element were found to improve the performance of gasoline in motor engines. But there was not enough bromine. So a great plant was erected on the Cape Fear peninsula, in North Carolina, to produce bromine by electrolyzing sea water. Bromine is present in sea water (in the form of bromides) to the extent of only 69 parts per million (1 pound in 2000 gallons); but this one plant produces about 2000 pounds of the element daily (Fig. 236). This plant has now been enlarged so that it has a capacity of about 50,000 pounds daily, and this can be increased if desired.

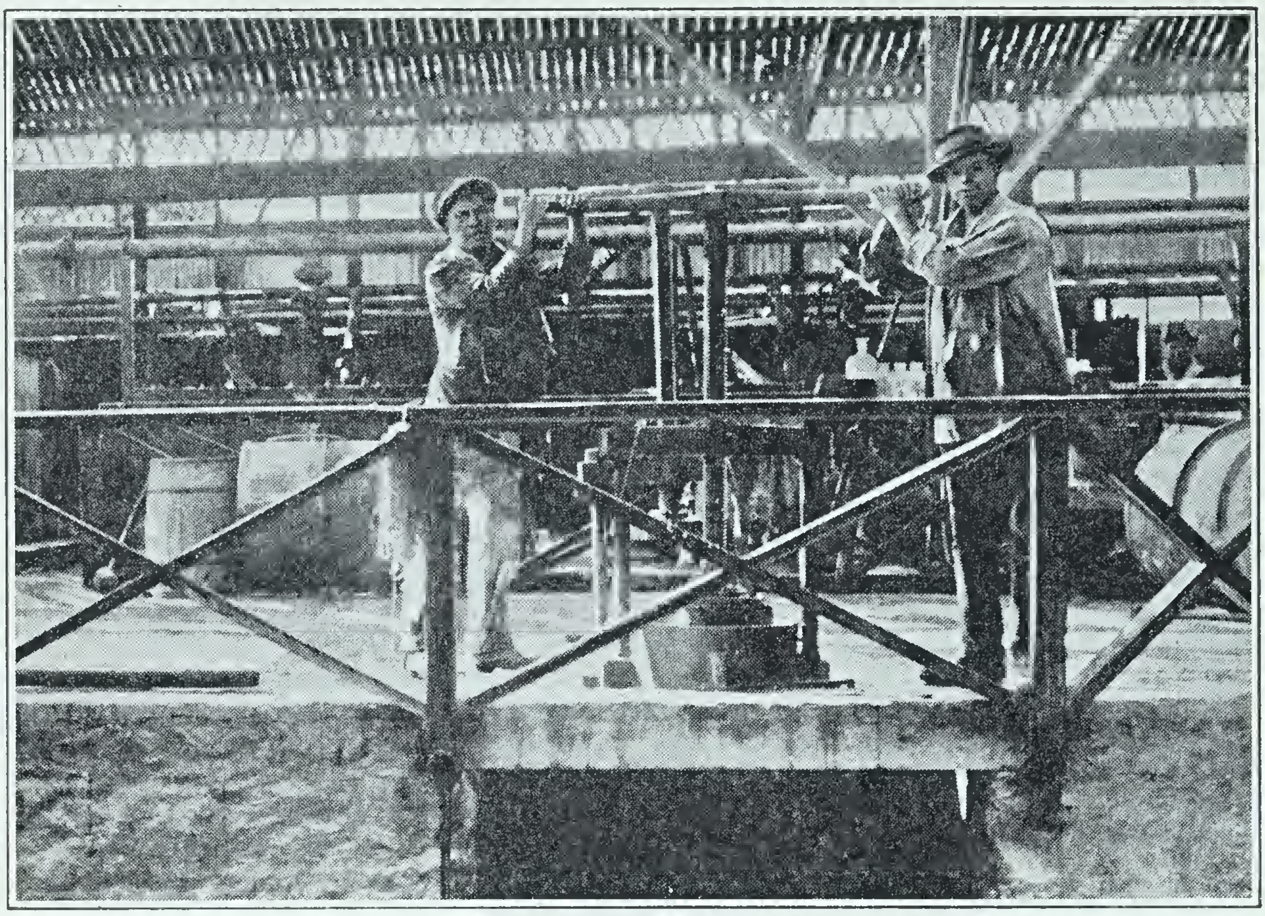
Hydrogen bromide (HBr); hydrobromic acid. Hydrogen bromide is a colorless gas resembling hydrogen chloride except that it is less stable. Its solution in water is hydrobromic acid. The salts of hydrobromic acid are called *bromides*. They resemble the chlorides in their properties.

Uses. At present the largest use of bromine is in the manufacture of ethylene bromide ($C_2H_4Br_2$), which is a constituent of "ethyl gasoline." It is also used in making many dyes and medicines and in the preparation of bromides. Silver bromide (AgBr) is used extensively in photography, while sodium bromide and potassium bromide are used as sedative drugs in the treatment of certain diseases. Bromine is also a constituent of several "tear gases."

IODINE

Some important facts about iodine. This element was discovered in compounds present in the ashes of sea plants by the French chemist Courtois in 1811. In appearance it differs from the other halogens in that it is a purplish-black, shining crystalline solid. When warmed it gives off a beautiful violet vapor, and it was this property that led Courtois to name the element *iodine*, a name derived from a Greek word meaning "violet-colored." It is nearly insoluble in water, but readily dissolves in carbon tetrachloride and in alcohol. It resembles chlorine and bromine in its chemical conduct, but is still less active than bromine. Even a trace of free iodine colors starch blue, a reaction which is used to detect the presence of either iodine or starch.

Like bromine, iodine occurs as an ion (I^-) in ocean water in very small *percentages*, but in a very large total quantity. It is absorbed from the water by certain sea plants, and is found in their ashes combined with metals. Certain of its compounds are also found in Chile saltpeter (p. 299). In very minute quantities it occurs in most natural waters and salt brines. The human body contains about 50 mg, one fifth of which is in the thyroid gland. In some instances, at



Iodine Educational Bureau, Inc.

FIG. 237. Compressing iodine into a convenient form for shipment

least, the disease of this gland known as *goiter* appears to be due to a deficiency of iodine.

Preparation of iodine. In the laboratory iodine is prepared in the same way as is bromine, using NaI in place of NaBr (p. 337). Commercially iodine was formerly obtained entirely from the ashes of seaweed (*kelp*), and a limited quantity still comes from this source. At present we get most of our supply from the beds of Chile saltpeter and from the gas-well brines of California and Louisiana (Fig. 237).

Hydrogen iodide (HI); hydriodic acid. Hydrogen iodide is a colorless gas, but is less stable than the corresponding compounds of the other halogens. Because of the ease with which it gives up hydrogen, it is a powerful reducing agent. Its solution in water is called *hydriodic acid*, and the salts of this acid are called *iodides*. In general these resemble the chlorides and bromides.

The uses of iodine. A solution of iodine and potassium iodide in alcohol is called *tincture of iodine* and is one of our most common antiseptics, as is also iodoform (CHI_3). Very finely divided iodine suspended in water is also used for this purpose. Silver iodide (AgI) is largely used in photography. Potassium iodide (KI) and many other iodine compounds are used in medicine, and iodine has many uses in chemical analysis.

The electromotive series of halogens. Just as the metals can be arranged in a series in which the higher ones displace the ions of the lower ones in the series (p. 261), so the halogen elements can be arranged in a similar series in the order fluorine, chlorine, bromine, iodine.

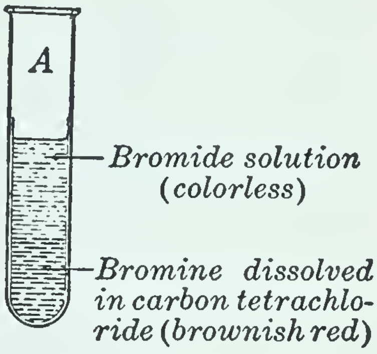

A
Bromide solution (colorless)
Bromine dissolved in carbon tetrachloride (brownish red)

FIG. 238. Testing for bromide ions or iodide ions

For example, chlorine gas bubbled into a solution having the ion Br^- or I^- takes away the excess electron from either of these ions and liberates them as free elements, itself becoming chlorine ions:

$$Cl_2 + 2\ K^+, Br^- \longrightarrow 2\ K^+, Cl^- + Br_2$$
$$Cl_2 + 2\ K^+, I^- \longrightarrow 2\ K^+, Cl^- + I_2$$

Test for bromide or iodide ions. As a test for the chloride ion we saw that a solution of silver nitrate, when added to a solution of a chloride, gives a white precipitate that is insoluble in nitric acid (p. 228). Unfortunately, bromides and iodides also give a precipitate with silver nitrate, and, while these precipitates (AgBr and AgI) are not entirely white, they may be so nearly so that we cannot distinguish the one from the other with certainty.

If we are uncertain as to whether the solid we are testing is a chloride, a bromide, or an iodide, we can easily distinguish between the three in the following way: Pour a few drops of the solution of the solid into a test tube half full of water, and add about 2 ml of carbon tetrachloride (Fig. 238). Next add a few drops of chlorine water and shake the mixture vigorously. If the solid being tested is a chloride, no reaction will take place; but if it is a bromide or an iodide, the element will be set free and will dissolve in the carbon tetrachloride. This solution soon settles to the bottom of the tube, colored brownish-red if bromine is present, and violet if iodine is there.

A more delicate test for *free* iodine consists in adding a little starch paste to the solution that may contain iodine. The starch is colored an intense blue by the iodine.

Properties of the halogens contrasted. By studying the table at the head of this chapter it will be seen that the halogens show a more or less regular gradation of properties. *This is a characteristic of a periodic family.* Each lacks one electron to complete its octet and so has a valence of -1. Fluorine is a light, slightly colored gas; chlorine is a heavier gas, with more marked color; while bromine is a red liquid, and iodine a nearly black solid. Their melting points *increase with their atomic weights* (see table). The stability of their compounds with hydrogen — HF, HCl, HBr, and HI — decreases as their atomic weights increase, HF being the most stable and HI the least so. There is some uncertainty as to whether bromine forms any oxides whatever, and the oxides of the other members of the family are unstable. Chlorine displaces bromine and iodine from their compounds with the metals, and bromine displaces iodine.

THE OXYGEN ACIDS OF THE HALOGENS, AND THEIR SALTS

With the exception of fluorine, each of the halogen elements forms several rather unstable acids with oxygen. A list of the chlorine acids is given on page 247. While these acids themselves are not very important, some of their salts have large uses. In general, the salts are formed by the action of the halogen element on an alkali.

Potassium chlorate ($KClO_3$). It will be recalled that we prepared oxygen in the laboratory by heating potassium chlorate. This is the potassium salt of chloric acid ($HClO_3$). It is made by the action of chlorine on hot solutions of potassium hydroxide. The reaction is somewhat complex, as is shown by the following equation:

$$3\,Cl_2 + 6\,KOH \longrightarrow 5\,KCl + KClO_3 + 3\,H_2O$$

It is a white crystalline substance, and is used chiefly as an oxidizing agent in the manufacture of matches, fireworks, and explosives. It is also used in the laboratory preparation of oxygen and in medicine. Sodium chlorate ($NaClO_3$) is prepared in this same way and is more soluble than the potassium salt.

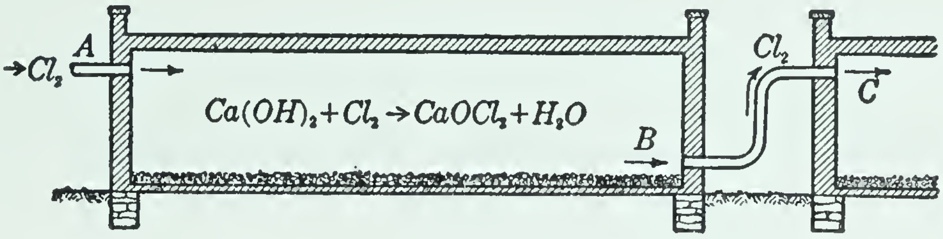


Fig. 239. Chambers for the manufacture of bleaching powder

Calcium hydroxide is spread to a depth of two or three inches upon the floor of a room made of lead or concrete. The chlorine enters near the top at *A* and reacts with the hydroxide. Any unabsorbed chlorine passes out at *B* and into the adjoining chamber at *C*. The commercial product ordinarily contains about 35 per cent of chlorine. It is shipped in sealed packages or iron drums

Bleaching powder. When chlorine is passed over solid calcium hydroxide, a white solid compound is formed having the formula $CaOCl_2$. This is called *bleaching powder*, *chloride of lime*, or simply *bleach*:

$$Ca(OH)_2 + Cl_2 \rightleftarrows CaOCl_2 + H_2O$$

When this compound is treated with an acid, chlorine is evolved:

$$CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2\uparrow$$

When exposed to the air, bleaching powder is slowly acted upon by moisture and carbon dioxide, evolving hypochlorous acid ($HClO$), an unstable compound, which is a good disinfectant. Bleaching powder is manufactured in large quantities (Fig. 239) and is used both as a disinfectant and as a bleaching agent, although for large-scale uses it is being replaced by liquid chlorine (p. 222).

CHAPTER SUMMARY IN QUESTION FORM

1. (*a*) Name the halogens. (*b*) Give the color and state of each.

2. Why are these elements called halogens?

3. (*a*) What compound of fluorine is very largely used in making electric-light bulbs? (*b*) Write the equation for its preparation.

4. Describe the process of etching glass.

5. Name two compounds which together will expel the three most familiar halogens from their salts.

6. (*a*) Illustrate question 5 by writing the equation for the laboratory preparation of bromine. (*b*) Substitute the symbol of iodine for that of bromine wherever it occurs in this equation; what does the equation now represent?

7. Do any of the halogens exist in a free state in nature?

8. What is the chief commercial source of bromine?

9. State the relation that bromine bears to (*a*) the automobile industry; (*b*) the movies.

10. Arrange on a sheet of paper the following table, inserting in vertical columns the information requested for the compounds HF, HCl, HBr, HI.

FORMULA	NAME	NAME OF WATER SOLUTION	NAME OF COMPOUND FORMED BY REPLACING H WITH K

11. Where in nature do we find most of (*a*) the iodide ions? (*b*) the non-ionized iodine?

12. Name the physical property by which you could easily identify (*a*) chlorine; (*b*) bromine; (*c*) iodine.

13. Write the names of the three most common halogens in the order in which the free element would displace the others from solutions of their salts.

14. A white or nearly white precipitate, insoluble in nitric acid, formed by adding a solution of silver nitrate to a solution indicates the presence of what ions?

15. Suppose you have a white solid, and know that it is either KCl, KBr, or KI. You could tell which of the three it is by dissolving the solid in water, adding first a few drops of carbon tetrachloride and then a few drops of chlorine water, and shaking the mixture well. What results would follow if the solid were (*a*) KCl? (*b*) KBr? (*c*) KI?

16. (*a*) Starch paste turns blue in the presence of what element? (*b*) So far as this test is concerned, does it make any difference whether the element is in a free state or a combined state?

17. What is the common name for a solution of a mixture of iodine and potassium iodide in alcohol?

18. Contrast the properties of the members of the chlorine family.

19. Have the members of the chlorine family a strong affinity for (*a*) hydrogen? (*b*) the metals? (*c*) oxygen?

20. State (*a*) the method of preparation, (*b*) the properties, and (*c*) the uses of potassium chlorate and of bleaching powder.

THOUGHT QUESTIONS

1. Some manufacturers of table salt advertise that their brand contains iodides. Why should this be considered a point worth advertising?

2. What gas have we studied that resembles the vapor of bromine? (*b*) How could you distinguish between the two?

3. Were any of the halogens known when oxygen was discovered?

4. Suppose you had potassium iodide and wished to prepare some tincture of iodine. How would you proceed?

5. (*a*) In which of the following would a reaction take place? (*b*) Complete the equations.

$KI + Cl$	$KBr + Cl$
$NaBr + I$	$NaCl + I$
$NaI + Br$	$KCl + Br$

6. Which of the following statements are true and which false? (*a*) The elements of the chlorine family show a regular gradation in their properties. (*b*) Bromine is the only element that is found in the liquid state under ordinary conditions. (*c*) Hydrogen chloride is more stable than hydrogen iodide. (*d*) Free chlorine passed into a solution of potassium iodide will liberate the iodine. (*e*) An iodine stain on one's hand can be removed by washing in water. (*f*) Tincture of iodine consists of a solution of iodine in alcohol.

7. Give the derivation (see dictionary) of each of the following names, and indicate whether or not the name is appropriate: (*a*) fluorine; (*b*) chlorine; (*c*) bromine; (*d*) iodine; (*e*) halogen.

8. What weight of potassium bromide would be required for the preparation of 25 g of bromine?

9. Suppose your hands were stained with iodine. How could you remove the stain?

10. Consult the table at the head of this chapter and draw diagrams to represent the structure of the atoms of each of the members of the chlorine family.

OPTIONAL EXERCISES

1. The tincture of iodine that you buy at the drug store contains 70 g of iodine and 50 g of potassium iodide dissolved in sufficient alcohol to make 1 liter of the solution. Suppose you had potassium iodide but no iodine with which to make the tincture. What weight of the salt would be required to prepare 1 liter of the tincture?

2. Demonstrate either or both of the following experiments before the class and explain fully what happens.

(*a*) Prepare some starch paste and divide it into two parts. Have at hand (1) a solution of iodine in alcohol, (2) a water solution of potassium iodide, and (3) some chlorine water. Ask the class to predict what will happen when starch paste is added to (1); to (2); to (3). See if their predictions are verified. Now add some chlorine water to (2) and account for the results.

(*b*) Place on a sheet of copper a piece of filter paper saturated with a solution containing potassium iodide and starch paste. Does a blue color appear? Attach the copper plate by a wire to the negative pole of a battery, and draw or write on the filter paper with one end of another wire attached to the positive pole of the battery. Explain the results.

UNIT READINGS

Beery. *Stuff.* [Read Chapter IV, entitled "The Wonders and the Horrors of the Halogens." Very interesting.]

Clarke. *Marvels of Modern Chemistry.* [Chapter XIII is entitled "The Red-Headed Halogens."]

Foster. *The Romance of Chemistry.* [Chapter XVI tells of the periodic table, isotopes, and heavy water. Chapter VIII tells of the halogens.]

Grosse. "A List of the Isotopes of the Elements," *Journal of Chemical Education*, Vol. XIV, pp. 436–442.

Harrow. *Eminent Chemists of Our Time.* [The story of Mendeléeff and his development of the periodic arrangement of the elements will be found on pages 19–40.]

Jaffe. *Crucibles.* [Chapter XI gives a very interesting biography of Mendeléeff.]

Weeks. *The Discovery of the Elements.* [Chapter XVII tells of the discovery of the halogens.]

Weeks. "The Periodic System of the Elements" and "Some Elements Predicted by Mendeléeff," *Journal of Chemical Education*, Vol. IX, pp. 1593–1602, 1605–1617.

Winicov. "Some of Mendeléeff's Personal Characteristics," *Journal of Chemical Education*, Vol. XIV, pp. 372–375.

The Science Leaflet. [For information about the periodic law, see Volume VIII, pp. 106–110; also Volume X, pp. 17–22. For discussion of heavy water, see Volume VII, pp. 315–317, and Volume VIII, pp. 111–115 and 799–804. For information about the chlorine family, see No. 4 of recent volumes.]

Unit Eight. Two Elements of Great Importance to Industry and Agriculture

SOME elements have important uses as uncombined elements. This is true of oxygen, hydrogen, chlorine, carbon, and many metals. Other elements are of little use in themselves, but give us many useful compounds. The two elements of this unit, sulfur and phosphorus, illustrate both these uses.

Something like two million tons of sulfur are mined in the United States annually. Free sulfur itself has some uses of which we shall learn in this unit. But whether we mine it as free sulfur or in the form of its compounds with metals (sulfides), we burn most of it to make the two oxides sulfur dioxide (SO_2) and sulfur trioxide (SO_3). Of these, sulfur dioxide itself has some uses; but both oxides find their greatest usefulness as the starting point in making sulfuric acid, which has a multitude of uses.

Every country in the world wants phosphorus. The element itself plays a small part in our lives, but we cannot get along without its compounds. We must have matches; we must have fertilizers, for our food must contain compounds of phosphorus, and the supply of this element in the soil must be renewed from time to time.

In this unit we shall study the two elements sulfur and phosphorus, and, more briefly, the three elements arsenic, antimony, and bismuth, near relatives of phosphorus.

CHAPTER XXX

Sulfur and Sulfides

[A Familiar Element with Many Important Compounds]

Why we must have sulfur. Most people know by sight the yellow solid called sulfur, but few realize its extreme importance to civilization. Free sulfur itself has not very many uses; it is its compounds that we need. We depend upon these for insecticides to protect fruits and vegetables from insect pests, for the refining of petroleum, and for the manufacture of soap, paper, rayon, matches, explosives for mining coal, dynamite for blasting rocks and making roads, rubber for automobile tires, and a host of other articles. It is a most important element.

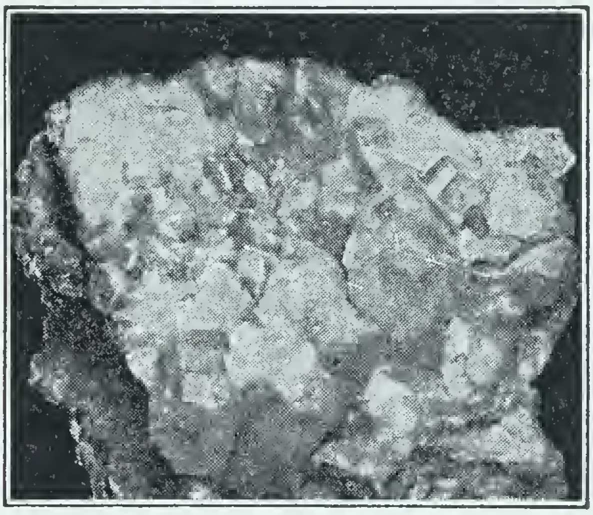


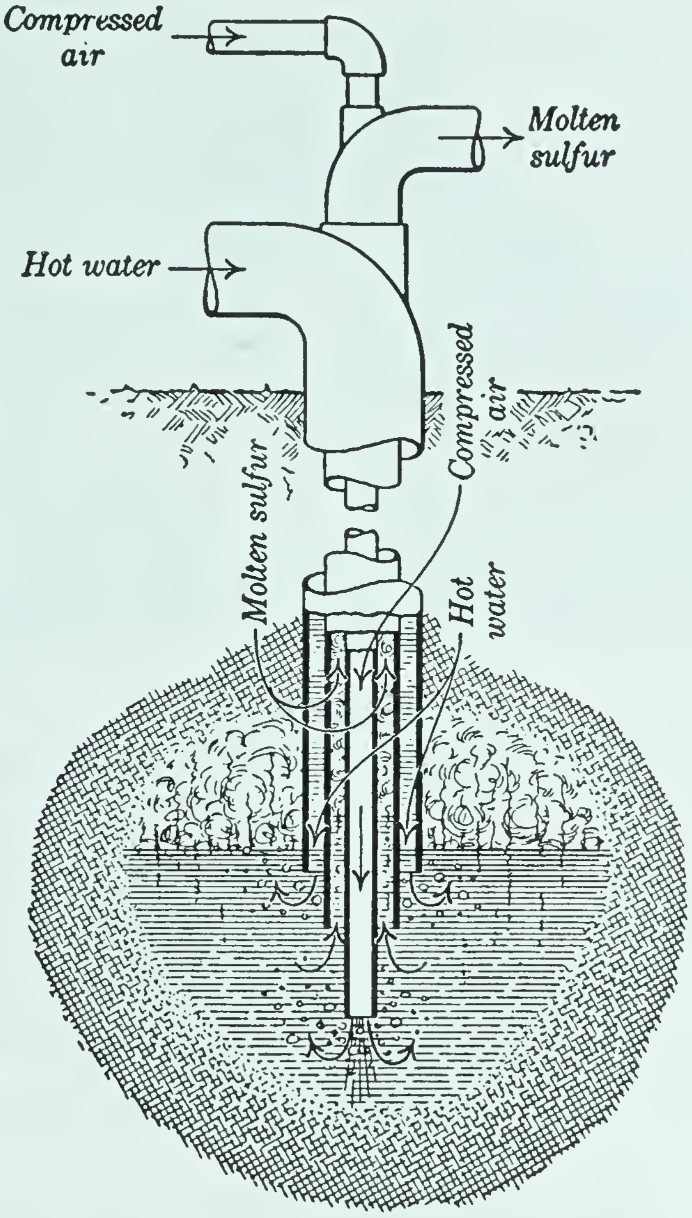
FIG. 240. Crystals of rhombic sulfur as they are found in nature

I. SULFUR

Sulfur is an old friend. Since sulfur is found in many places uncombined, and burns very easily, it is one of the elements known from very early times. It is the brimstone of the Bible; it played a notable part in the speculations of the alchemists about the nature of matter.

Nearly every country has sulfur in some form. Sulfur is widely distributed in nature and occurs in large quantities in the free state, especially in the neighborhood of volcanoes. It is sometimes found in well-formed crystals (Fig. 240). The United States is by far the greatest sulfur-producing country, and Texas and Louisiana produce approximately 99 per cent of its output. The mines of Sicily have been worked for centuries, and Japan, Chile, and Spain have rich deposits.

Combined with metals as *sulfides* and *sulfates*, sulfur is very abundant. In smaller quantities it is found in a great



A large tube is driven down into the deposit, and inside this are placed two pipes, one inside the other. Through one pipe, water heated under pressure to about 180° is forced, and hot air through the other pipe. The hot water melts the sulfur, and the air forms a froth of low density. The pressure of the water and air forces the melted sulfur up through the space shown in the figure, so that a continuous flow of molten sulfur comes from the pipe. A single well can produce 500 tons of sulfur (99.5 per cent pure) daily

Fig. 241. A diagram of the Frasch process for producing sulfur

variety of minerals and in many vegetable and animal substances, especially in eggs and mustard oil.

How we get sulfur. In Texas (and in Louisiana) the sulfur is found in deposits far underground, and is covered with quicksand so that it cannot be mined like coal. A typical deposit lies at a depth of 700 feet; it is circular in shape, and is about half a mile in diameter and 500 feet in thickness. For years there seemed to be no way to get at these vast stores of sulfur, but about 1900 the American engineer Frasch solved the problem in a very ingenious way (Figs. 241 and 242).

Distillation of sulfur. Before the Frasch process was invented, crude sulfur was imported from Sicily and purified by distillation (Fig. 243). When the sulfur vapor first comes

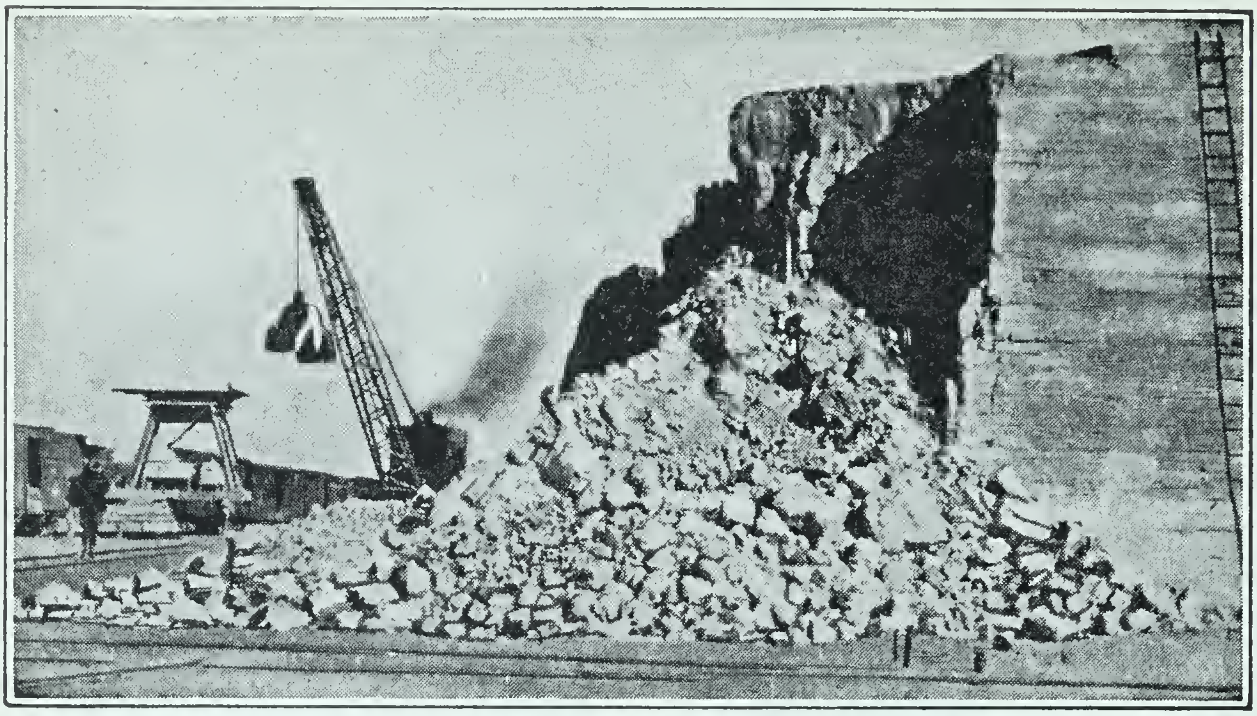


FIG. 242. A block of sulfur at the mine

In the Frasch process the sulfur flows into wooden forms and solidifies

into the cold condensing room, it condenses as a fine crystalline powder called *flowers of sulfur*, just as water vapor often condenses to frost or snow. As the condensing room becomes warm the sulfur condenses as a liquid, and is drawn off into cylindrical molds to solidify, the product being called *roll sulfur* or *brimstone.*

Some properties of sulfur. Ordinary sulfur is a pale-yellow solid without marked taste and with but a faint odor. It is a nonconductor of electricity, is insoluble in water, but is freely soluble in a few liquids, especially in carbon disulfide.

When melted it forms a thin, straw-colored liquid. If this liquid is now heated carefully, it turns darker in color as the temperature is raised, and becomes thicker until at about 235° it is almost black and is so thick that the vessel holding it can be turned upside down without danger of having the liquid run out. At higher temperatures it becomes thin once more, but is still very dark. It boils at 444.6°, giving a yellowish vapor. When the vapor liquefies, the same changes take place in the reverse order.

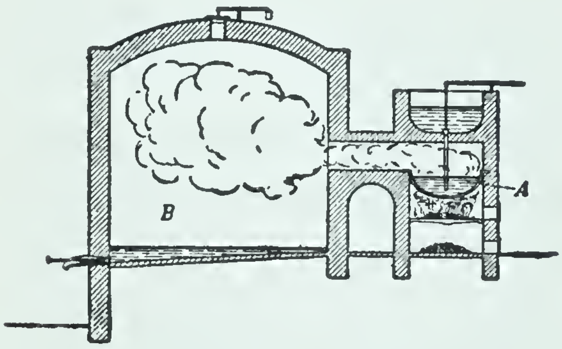


FIG. 243. Diagram of a sulfur still

Varieties of sulfur. Sulfur is known in a number of quite different (allotropic) varieties. Many other elements occur in different forms (p. 97); but sulfur has more than most elements, and they are easy to get. The best-known are the following:

1. ***Rhombic, or ordinary, sulfur.*** When sulfur crystallizes from solution in liquids (notably in carbon disulfide), it makes compact yellow crystals which melt at 112.8°. This is called *rhombic sulfur.* Brimstone and the crystals found in nature are composed largely of this variety (Fig. 240). It is the most stable form of sulfur at all ordinary temperatures.

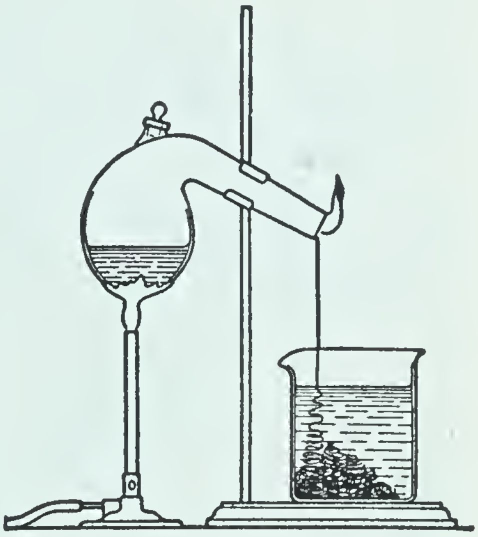


Fig. 244. Preparation of plastic sulfur

Sulfur is distilled, and the condensed liquid chilled in water

2. ***Prismatic, or monoclinic, sulfur.*** When melted sulfur is allowed to cool until a part of the liquid has solidified, and the remaining liquid is then poured off, it is found that the solid sulfur remaining in the vessel is in the shape of fine needlelike crystals which melt at 119.2°. This form is called *prismatic* or *monoclinic sulfur.* At all temperatures below 96° the needle-shaped crystals break up more or less rapidly into little crystals of the rhombic variety.

3. ***Plastic sulfur.*** When boiling sulfur is slowly poured into cold water, it makes gummy, doughlike strings which can be stretched into threads (Fig. 244). It is simply undercooled (p. 55) liquid sulfur. It gradually passes over into ordinary rhombic sulfur.

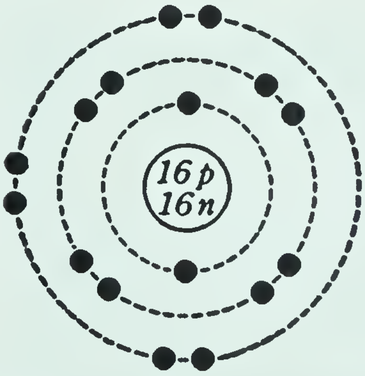


Fig. 245. The structure of the sulfur atom

The chemical conduct of sulfur. The sulfur atom, like the oxygen atom, has six valence electrons and needs two more to complete its valence orbit (Fig. 245). It can do this by forming compounds with atoms somewhat like itself or by capturing the extra electrons from atoms that have only one or two in their valence orbit, like hydrogen or the metals.

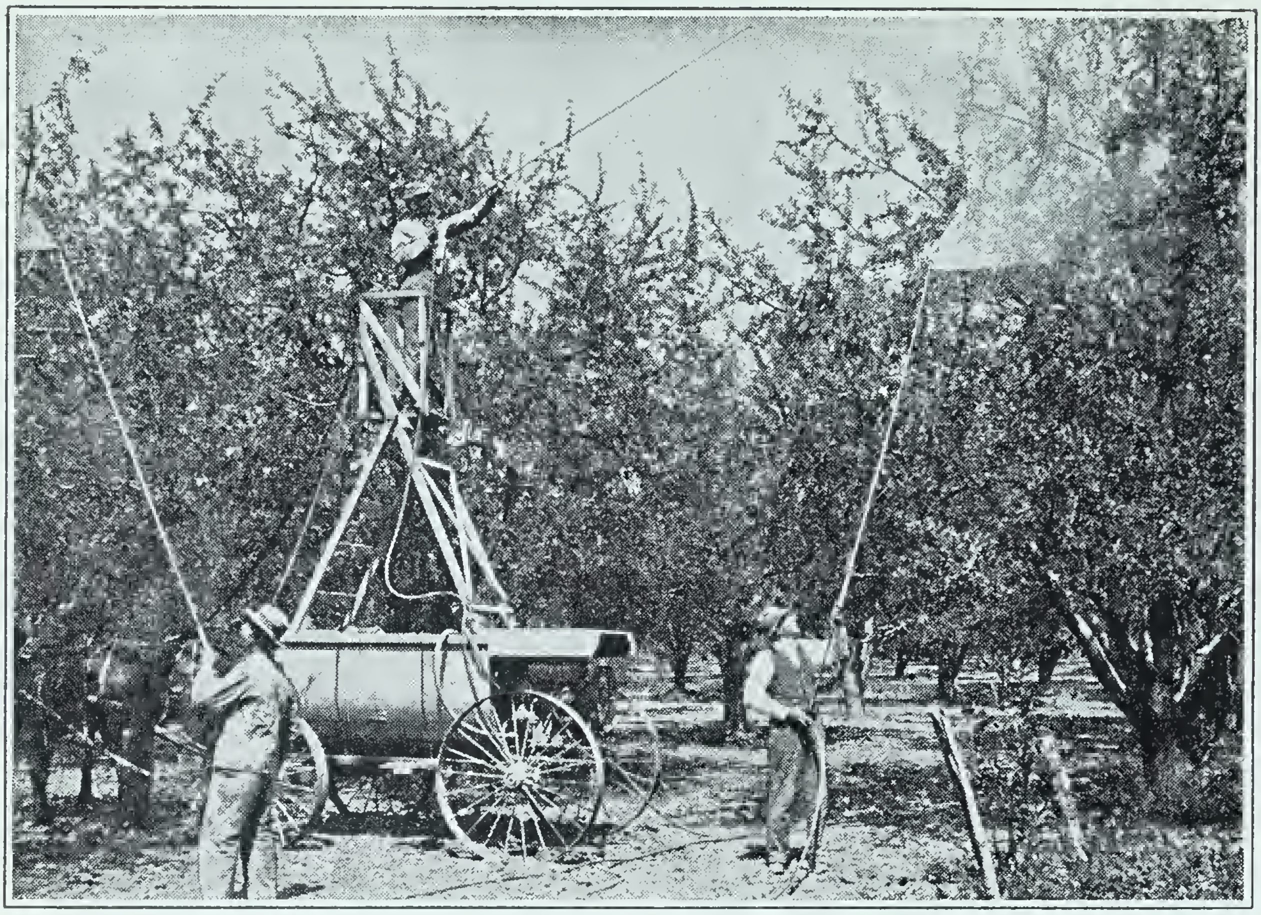


FIG. 246. Spraying an orchard of fruit trees with lime-sulfur spray

It burns in oxygen or the air to make covalent sulfur dioxide, SO_2. When heated with certain metals, such as iron or copper or zinc, it captures two electrons from them and forms metallic sulfides. In some cases the action is so vigorous that the mass becomes red-hot, as is the case with iron. This conduct recalls the action of oxygen upon metals, and in general the metals which react readily with oxygen are apt to combine with sulfur. With much less ease sulfur combines with many nonmetals, such as chlorine and carbon, to make covalent compounds.

Lime-sulfur spray. There are many chemical insecticides, the chief one containing sulfur being called *lime-sulfur spray.* It is made by boiling sulfur with slaked lime, $Ca(OH)_2$, which makes a deep-red liquor that is essentially a solution of sulfides of calcium (CaS_4 and CaS_5). The liquid is a very effective insecticide, particularly for scale, and it is also a fungicide (to kill fungi or molds) (Fig. 246). Flowers of sulfur is often used in the shape of dust as a fungicide, not because it is itself poisonous but because with air and water it slowly produces poisonous compounds.

II. THE SULFIDES

Hydrogen sulfide (H_2S) — properties. With hydrogen, sulfur forms the important compound called *hydrogen sulfide* (H_2S). This is a colorless gas having a weak, disagreeable taste and a most unpleasant odor, suggesting rotten eggs, which, in fact, owe their odor to it. Under ordinary conditions (1 atmosphere and 20°) it is not very soluble in water, 100 volumes of water dissolving 290 volumes of the gas. In boiling water it is not soluble at all. When inhaled in concentrated form it is a violent poison, and even when much diluted with air it causes headache, dizziness, and nausea. Great caution must consequently be used in working with it. Fortunately its odor gives warning of its presence.

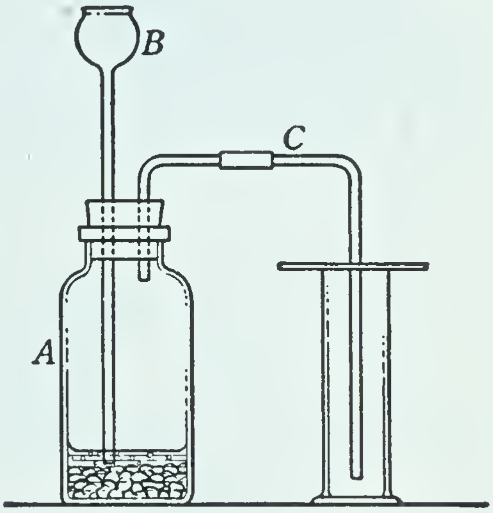


FIG. 247. Preparation of hydrogen sulfide

Iron sulfide is placed in flask *A*, and hydrochloric acid is added through *B*. Hydrogen sulfide escapes through *C* and is collected by displacement of air

Hydrogen sulfide in nature. Hydrogen sulfide is sometimes noticed in the vapors coming from volcanoes. It occurs also in solution in many natural waters (*sulfur waters*). It is formed in the decay of organic matter containing sulfur, just as ammonia is formed from nitrogenous matter.

How hydrogen sulfide is made. Since hydrogen sulfide is a gas which is but slightly soluble in water, it can be prepared *by treating a sulfide with an acid.* Iron sulfide (FeS) is generally used (Fig. 247):

$$FeS + 2\,HCl \longrightarrow FeCl_2 + H_2S\uparrow$$

How hydrogen sulfide acts. The most important chemical reactions of hydrogen sulfide are the following:

1. ***Acid properties.*** When dissolved in water, hydrogen sulfide acts as a very *weak acid* (p. 259), the solution being sometimes called *hydrosulfuric acid.*

2. ***Action with oxygen.*** The elements composing hydrogen sulfide are not held together very firmly, and have each a

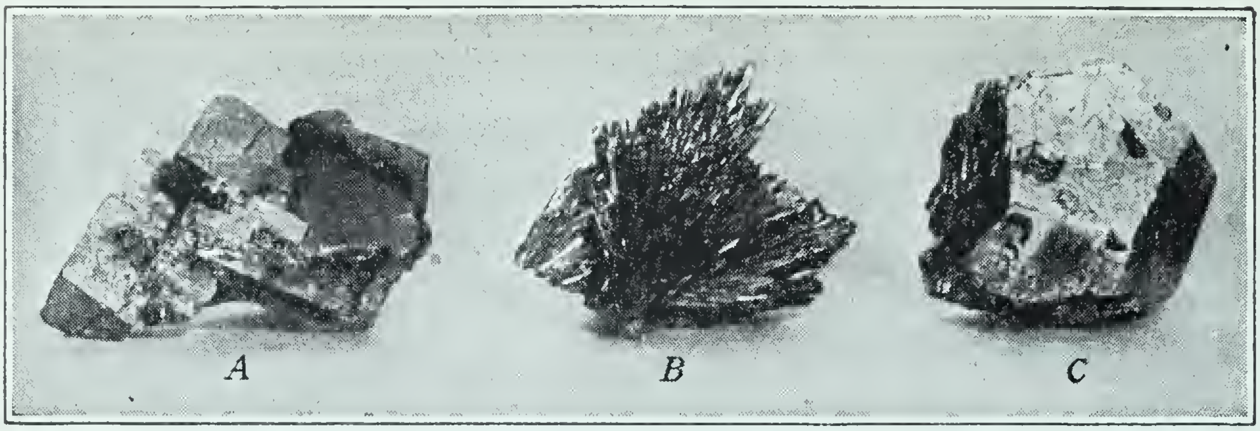


FIG. 248. Some mineral sulfides

A, lead sulfide, PbS (galenite); *B*, antimony sulfide, Sb_2S_3 (stibnite); *C*, iron disulfide, FeS_2 (pyrite, fool's gold)

strong affinity for oxygen. So the gas burns readily in oxygen or air according to the equation

$$2\,H_2S + 3\,O_2 \longrightarrow 2\,H_2O + 2\,SO_2$$

When there is not enough oxygen for both the sulfur and the hydrogen, or when the temperature is kept low, the hydrogen combines with the oxygen, and the sulfur is set free:

$$2\,H_2S + O_2 \longrightarrow 2\,H_2O + 2\,S$$

It is probable that some of the free sulfur in volcanic regions is due to this reaction.

3. ***Reducing action.*** Because of the ease with which hydrogen sulfide decomposes and the strong tendency of both sulfur and hydrogen to combine with oxygen, the substance is a strong *reducing* agent.

4. ***Action on metals.*** Because of its unstable character and the affinity of sulfur for the metals, hydrogen sulfide acts on many of the metals, not as an acid, but as a sulfurizing agent. In this way the hydrogen sulfide in the air acts on silver, forming black silver sulfide, which tarnishes the metal.

Sulfur waters. The waters of many natural springs hold hydrogen sulfide in solution, as is shown by their strong odor and the way in which they will blacken a silver coin. When the water reaches the air, the hydrogen sulfide is slowly oxidized, with the liberation of sulfur, which often deposits about the borders of the spring.

Salts of hydrosulfuric acid; sulfides. The salts of hydrosulfuric acid (called *sulfides*) are an important class of compounds. Nearly all the heavier metals are found in nature chiefly as sulfides, and much of the sulfur of the world is combined with iron as iron disulfide (FeS_2). Most of the copper, lead, zinc, and silver of commerce is produced from mineral sulfides (Fig. 248). As we have seen, lime-sulfur spray is largely composed of sulfides of calcium.

In their formulas the sulfides closely resemble the oxides, just as H_2S resembles H_2O.

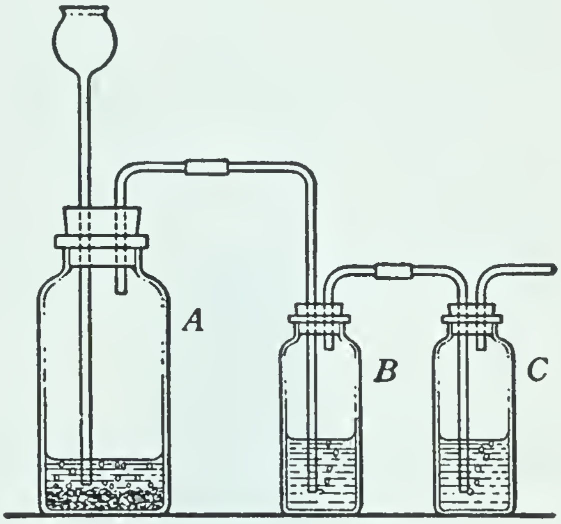


FIG. 249. Preparation of insoluble sulfides

Hydrogen sulfide is generated in flask *A* and passed into solutions of salts in bottles *B* and *C*

Uses of the sulfides in analysis. Most of the sulfides are insoluble in water, and some of them are insoluble in acids. So when hydrogen sulfide is bubbled through a solution of a salt, it often happens that a sulfide is precipitated (Fig. 249). With copper chloride the equation is

$$CuCl_2 + H_2S \longrightarrow CuS\downarrow + 2\ HCl$$

Some sulfides are precipitated from an acid solution, and some from an alkaline or neutral solution, while others are soluble and do not precipitate at all. They have a striking variety of colors. Many are black; others are yellow, orange, pink, or white.

For these reasons hydrogen sulfide is much used in chemical analysis in separating and identifying the metal ions present in a solution.

Test for the sulfide ion. Hydrosulfuric acid and all soluble sulfides give sulfide ions, S^{--}, in solution. If we wish to test for the presence of this ion, we simply add to its solution the salt of some metal that forms an *insoluble* sulfide of characteristic color. A silver salt produces a *black* precipitate of silver sulfide (Ag_2S), which shows the presence of S^{--} ions:

$$2\ AgNO_3 + H_2S \longrightarrow Ag_2S\downarrow + 2\ HNO_3$$

Carbon disulfide (CS_2). When sulfur vapor is passed over hot carbon, the two elements combine, forming *carbon disulfide* (CS_2), just as oxygen and carbon unite to form carbon dioxide (CO_2) (Fig. 250). The compound is a heavy, colorless liquid having a pleasant odor when pure. On standing, especially in sunlight, it gets a most disagreeable odor, because of a slight decomposition. *It is a very good solvent for many substances, such as gums, rubber, waxes, and fats, which are insoluble in most liquids.* It boils at a low temperature (46°), and its vapor is not only very poisonous but very inflammable. It is made in considerable quantities for use as a solvent in the manufacture of rayon; as an insecticide (especially to kill white ants); and in the manufacture of carbon tetrachloride, which is used as a fire extinguisher (p. 154) and in dry cleaning.

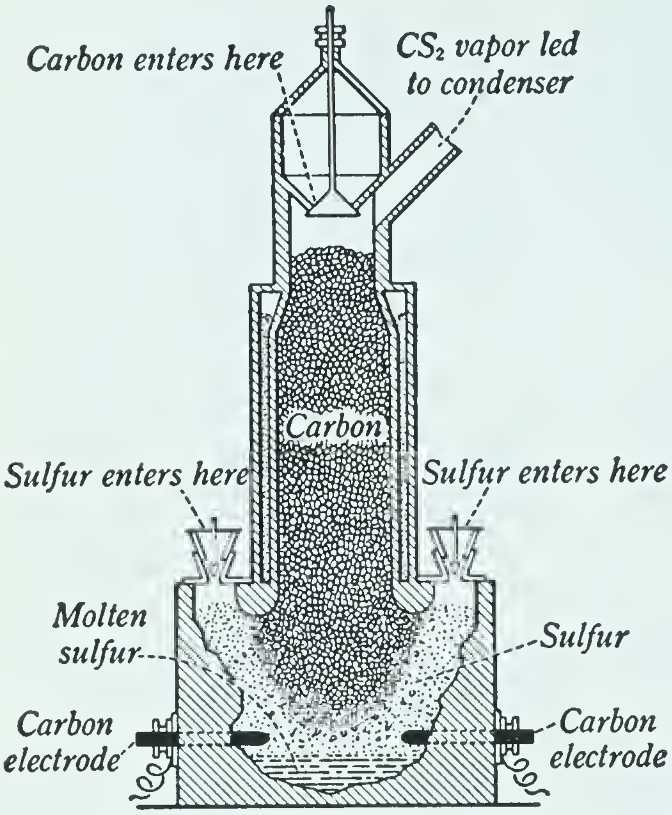


FIG. 250. The manufacture of carbon disulfide

Heat is generated by an electric current as shown in the figure. The sulfur is vaporized and, passing up through the hot carbon, unites with it to form the vapor of carbon disulfide. The vapor is liquefied by passing it through condensers

Selenium and tellurium, two near relatives of sulfur. Sulfur has two near relatives, namely, selenium and tellurium. Not only are these elements similar to sulfur but their compounds are closely related to the corresponding compounds of sulfur. They are not abundant elements and have few uses. Selenium is used to some extent in certain electrical appliances, and in giving red color to glass. Much of the red glass used in the taillights of automobiles is colored by selenium.

Selenium compounds are poisonous. Some plants growing on soils containing selenium take it up, as on our dry Western plains, where thousands of sheep and cattle have died from eating these poisonous plants. The cattlemen call the symptoms of this poisoning blind staggers or alkali poisoning. Selenium is the only known case of a poisonous inorganic substance taken from the soil by plants in poisonous quantities.

CHAPTER SUMMARY IN QUESTION FORM

1. Name the countries that have the largest deposits of sulfur.

2. (*a*) In what form does sulfur occur in nature? (*b*) Is there any in our bodies? (*c*) If so, calculate the weight of sulfur in your body (see page 30).

3. (*a*) Why cannot the sulfur in Texas and Louisiana be mined like coal? (*b*) Who finally devised a way of obtaining this sulfur? (*c*) Explain the process of obtaining it.

4. Two common varieties of sulfur on the market are *flowers of sulfur* and *brimstone.* (*a*) How is each obtained? (*b*) How do they differ in appearance?

5. Give the changes which sulfur undergoes when it is heated from room temperature to its boiling point.

6. (*a*) Name the three allotropic forms of sulfur, and (*b*) state how each can be formed. (*c*) Which is the most stable form?

7. (*a*) Name a liquid in which sulfur is soluble, and (*b*) give the form of sulfur that remains when the solution is evaporated.

8. What compound is formed when sulfur combines (*a*) with oxygen? (*b*) with a metal such as iron?

9. (*a*) What is the composition of *lime-sulfur spray*? (*b*) How is it prepared? (*c*) For what is it used?

10. In the preparation of hydrogen sulfide give (*a*) the name of the compounds used; (*b*) the products of the reaction; (*c*) the equation for the reaction; (*d*) the methods of collecting the gas.

11. Write a descriptive paragraph on hydrogen sulfide, giving its physical state, its odor, its action on the body when inhaled, its solubility in water, and its weight compared with air.

12. (*a*) What is the difference between hydrogen sulfide and hydrosulfuric acid? (*b*) What are the salts of hydrosulfuric acid called?

13. Hydrogen sulfide burns when ignited in air. Write the equation for its combustion (*a*) when there is plenty of air; (*b*) when the supply of air is limited.

14. (*a*) What compounds give the sulfide ion S^{--} in solution? (*b*) How can you test for the presence of this ion?

15. What are (*a*) the uses of selenium? (*b*) its dangers?

THOUGHT QUESTIONS

1. Iron disulfide (FeS_2) is a mineral called "fool's gold" because it looks like gold. How could you tell it from gold?

2. (*a*) Name the elements so far studied that occur in allotropic forms. (*b*) Give the names of the different forms.

3. Suppose you were to grind a part of a stick of sulfur to a fine powder. Would the powder and the stick be allotropic forms of sulfur?

4. How could you tell whether any two forms of an element are allotropic forms of the element or simply different physical states of the same form?

5. The reaction used in the preparation of hydrogen sulfide is a reversible one. (*a*) Does it complete itself? (*b*) Why?

6. Hydrogen sulfide is as poisonous as carbon monoxide; yet we do not fear it as we do carbon monoxide. Why?

7. We often hear of "sulfur waters" and "sulfur springs"; yet sulfur is insoluble in water. Explain.

8. When ignited, carbon disulfide burns in air, both of the elements present being completely oxidized. Write the equation for the reaction.

OPTIONAL EXERCISES

1. Calculate (*a*) the number of liters of oxygen required to burn 10 liters of hydrogen sulfide, and (*b*) the number of liters of sulfur dioxide formed.

2. Consult the table of solubilities (Appendix D) and note sulfides that are soluble in water. Predict what will happen when hydrogen sulfide is passed into solutions of each of the following compounds, writing the equations for any reactions that may occur, and indicating by the usual sign those compounds that are precipitated: (*a*) silver nitrate ($AgNO_3$); (*b*) copper sulfate ($CuSO_4$); (*c*) sodium chloride; (*d*) potassium hydroxide; (*e*) lead nitrate ($Pb(NO_3)_2$).

3. Prepare a table giving the following information concerning the elements we have so far studied:

NAME OF ELEMENT	PHYSICAL STATE	COLOR	ODOR	SOLUBILITY IN WATER	WILL IT BURN?

CHAPTER XXXI

The Oxides of Sulfur and Their Acids

[Two Compounds with Important Near Relatives]

I. SULFUR DIOXIDE; SULFUROUS ACID

Sulfur dioxide, or sulfurous anhydride (SO_2). Sulfur is almost without odor, but when it burns we notice a peculiar and very irritating odor. This is the odor of sulfur dioxide. This compound is a colorless gas about twice as heavy as air. It is easily liquefied by a pressure of about three atmospheres or, under ordinary pressure, by cooling it in a freezing mixture of ice and salt (Fig. 251). In the liquid state it is sold on the market in metal or strong glass containers, and for use in larger quantities it is often shipped in tank cars, like gasoline (Fig. 252).

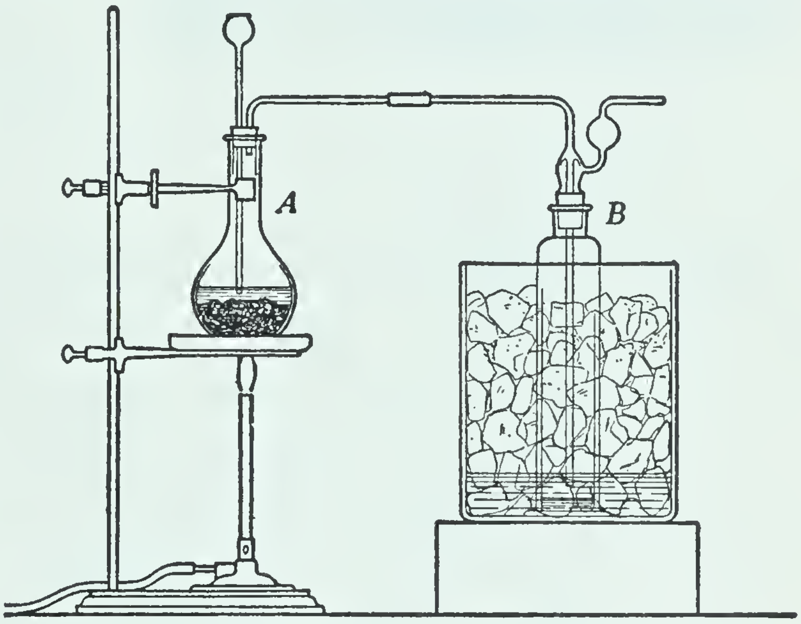


FIG. 251. Sulfur dioxide gas is easily liquefied

The gas is generated in *A* and conducted into a vessel *B* surrounded by a freezing mixture of ice and salt

How we get sulfur dioxide. It is possible to prepare sulfur dioxide by several methods. The following two ways are those ordinarily used:

1. ***By burning sulfur.*** When wanted in large quantities for commercial uses, it is made by burning sulfur or the sulfides of certain metals:

$$S + O_2 \longrightarrow SO_2\uparrow$$
$$2\ ZnS + 3\ O_2 \longrightarrow 2\ ZnO + 2\ SO_2\uparrow$$

Coal almost always contains sulfur compounds, and when such coal is burned, sulfur dioxide is formed. We often notice the irritating odor of the dioxide when breathing the air in an enclosed railway station.

2. *By the action of an acid on the salt of sulfurous acid (sulfite).* It will be recalled (p. 248) that when a carbonate is treated with an acid, carbon dioxide is set free:

$$Na_2CO_3 + 2\,HCl \longrightarrow 2\,NaCl + H_2O + CO_2\uparrow$$

In a similar way, when a sulfite is treated with an acid, sulfur dioxide is given off:

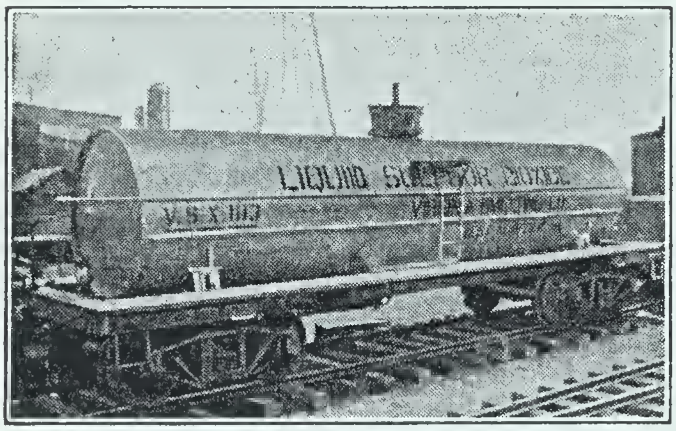


FIG. 252. Tank car of liquid sulfur dioxide

$$Na_2SO_3 + 2\,HCl \longrightarrow 2\,NaCl + H_2O + SO_2\uparrow$$

Some reactions that sulfur dioxide undergoes. Sulfur dioxide has a strong tendency to combine with other substances, as, for example, with both chlorine and oxygen. It can even take oxygen away from some other compounds and is therefore a good reducing agent. It combines readily with water to form sulfurous acid (H_2SO_3).

Some uses of sulfur dioxide. Some sulfur dioxide is used in making sulfurous acid and its salts. Its greatest use is in the manufacture of sulfuric acid, as will be explained later.

Sulfurous acid (H_2SO_3). When sulfur dioxide is passed into water, a chemical equilibrium results between sulfur dioxide and water, on the one hand, and sulfurous acid, on the other:

$$H_2O + SO_2 \rightleftarrows H_2SO_3$$

It is not possible to prepare this acid in pure condition, because it breaks down easily into water and sulfur dioxide. Any attempt to evaporate the solution drives off the sulfur dioxide, and the equilibrium is disturbed. Solutions of the acid in water have a number of interesting properties and commercial uses.

1. *Acid properties.* The solution has all the properties of a very weak acid.

2. *Reducing properties.* Solutions of sulfurous acid act as good reducing agents. This is because sulfurous acid has the

power of taking up oxygen from the air, or from substances in which oxygen is held rather loosely, and is changed by this reaction into sulfuric acid:

$$2\ H_2SO_3 + O_2 \longrightarrow 2\ H_2SO_4$$

3. ***Bleaching properties.*** Sulfurous acid has bleaching properties, although it is not as good a bleaching agent as chlorine (p. 223). It is used to bleach materials that would be injured by the action of chlorine, such as silk, straw goods, feathers, and even such foods as canned corn and dried fruits. Bleaching is often accomplished by merely exposing the *wet* material to the fumes of burning sulfur (Fig. 253). As a rule the bleaching is not permanent, the color returning with exposure to air and sunshine, as in the case of a straw hat that has been bleached.

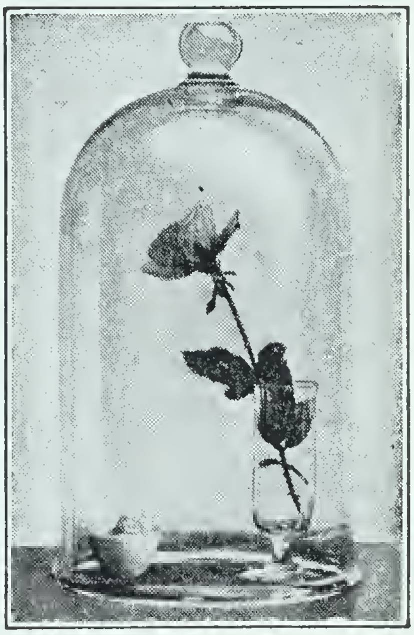


FIG. 253. Bleaching a moist flower with sulfur fumes

Salts of sulfurous acid — sulfites. The sulfites are solid salts. Like sulfurous acid they have the power of taking up oxygen very readily, forming sulfates, and are good reducing agents as well as bleaching agents. On account of this tendency commercial sulfites are often contaminated with sulfates. The bisulfite of calcium, $Ca(HSO_3)_2$, is used in great quantities in the manufacture of paper from wood, since it dissolves the gluelike material that holds the wood cells together and leaves the pure cellulose (paper material). The bisulfite is made by passing sulfur dioxide into a solution or suspension of calcium hydroxide:

$$H_2O + SO_2 \longrightarrow H_2SO_3$$
$$Ca(OH)_2 + 2\ H_2SO_3 \longrightarrow Ca(HSO_3)_2 + 2\ H_2O$$

II. SULFUR TRIOXIDE; SULFURIC ACID

Sulfur trioxide, or sulfuric anhydride (SO_3). Sulfur trioxide is a colorless liquid which freezes at about 15° and boils at 46°. A trace of moisture causes it to solidify into a mass of silky white crystals which look much like asbestos. In contact with air, sulfur trioxide fumes strongly, and when thrown upon water it dissolves with a hissing sound and the liberation of a great deal of heat. The product of the reaction is sulfuric acid, so that sulfur trioxide is the anhydride of that acid (p. 303):

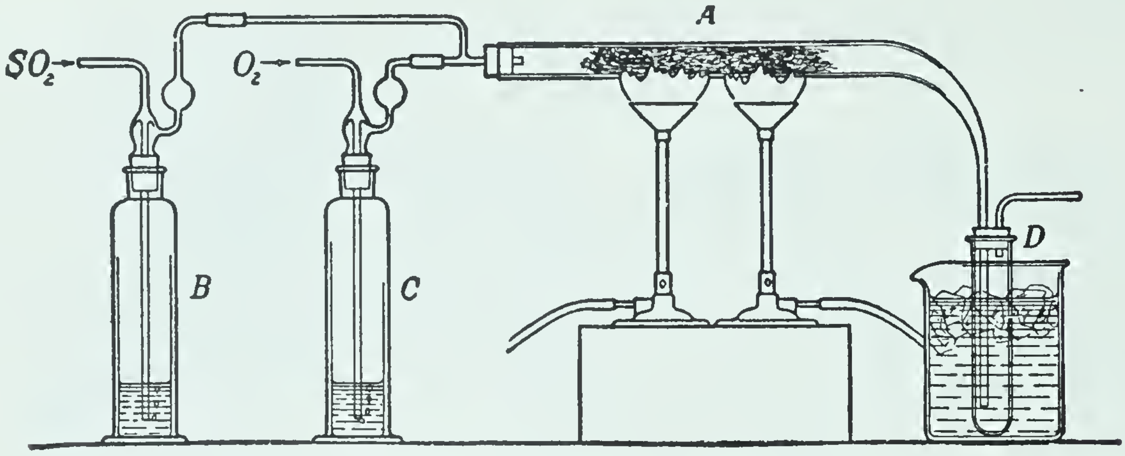


FIG. 254. The preparation of sulfur trioxide

Sulfur dioxide and oxygen, dried by bubbling through concentrated sulfuric acid in *B* and *C*, are together passed over the heated catalyst in *A*. The resulting sulfur trioxide condenses in *D*

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

How sulfur trioxide is made. When sulfur dioxide and oxygen are heated together at a rather high temperature, a small amount of sulfur trioxide is formed, but the reaction is slow and incomplete. If, however, a suitable catalytic agent, such as finely divided platinum, is present (Fig. 254), the reaction is rapid and nearly complete:

$$2\ SO_2 + O_2 \longrightarrow 2\ SO_3$$

Sulfuric acid (H_2SO_4), the "king of chemicals." Strictly speaking, sulfuric acid is a solution of hydrogen sulfate (H_2SO_4) in water. But both hydrogen sulfate and its solution in water are called *sulfuric acid.* The pure compound is a colorless liquid nearly twice as heavy as water. The ordinary concentrated acid sold on the market contains about 2 per cent of water, has a density of 1.84, and boils at 338°. It is sometimes called *oil of vitriol.*

Sulfuric acid is one of the most important of all manufactured chemicals. Next to water it is the liquid most used in chemical industries. Large quantities are prepared for use in the manufacture of fertilizers, in petroleum refining, in dissolving the oxidized scale from metals in the iron and steel industry, and in the manufacture of many other important materials, including dyes, paints and pigments, explosives, rayon and cellophane, and various chemicals (Fig. 255).

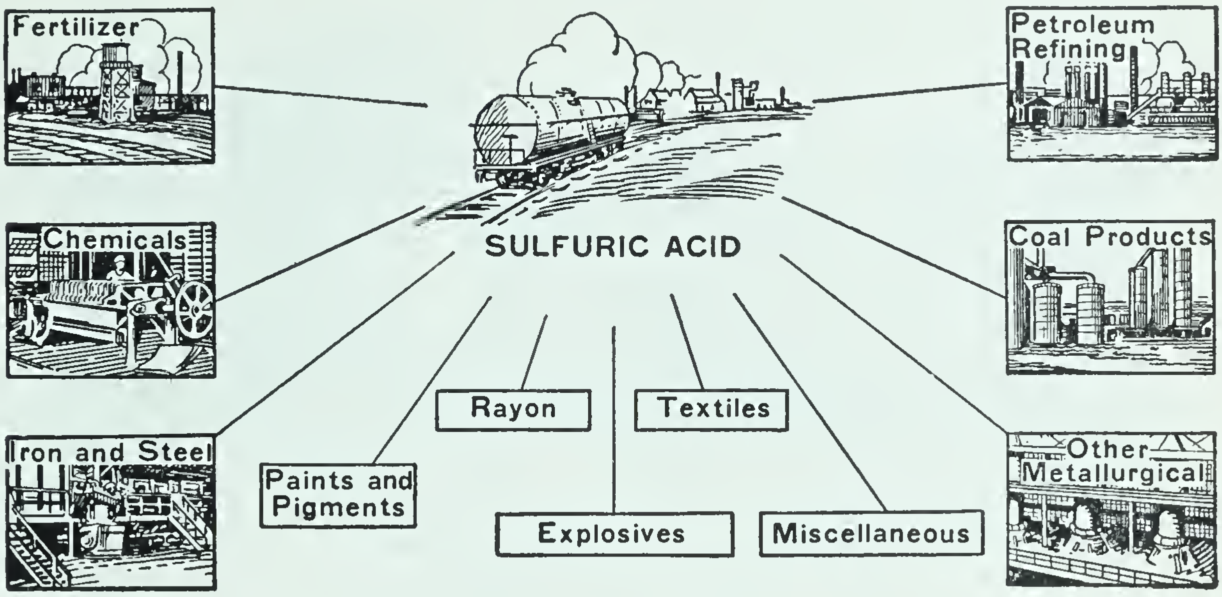

Fertilizer
Petroleum Refining
Chemicals
SULFURIC ACID
Coal Products
Rayon
Textiles
Iron and Steel
Paints and Pigments
Other Metallurgical
Explosives
Miscellaneous

FIG. 255. The important uses of sulfuric acid

The two common ways of making sulfuric acid. Sulfuric acid can be made at low cost and is the cheapest of commercial acids. Two general methods are used in its manufacture.

1. ***The contact process.*** In this process sulfur trioxide is first made from sulfur dioxide and oxygen by the use of a catalyst, as explained in Fig. 254. The sulfur dioxide is obtained by burning sulfur. The catalyst used is either platinum or compounds of the element vanadium. The resulting sulfur trioxide is brought into contact with water, with which it unites to form sulfuric acid:

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

The contact process produces pure concentrated acid (Fig. 256), and this is the kind demanded by most of the industries requiring sulfuric acid. Even in those using the dilute acid it is often cheaper to buy the concentrated acid and dilute it as required than to pay freight on the water present in the dilute acid.

2. ***The chamber process.*** Until recent years, when the contact process first came into use, all sulfuric acid was made by the "chamber process." While this process is much more

complicated than the contact process, it is still largely used. It is based on the reaction of water, sulfur dioxide, and

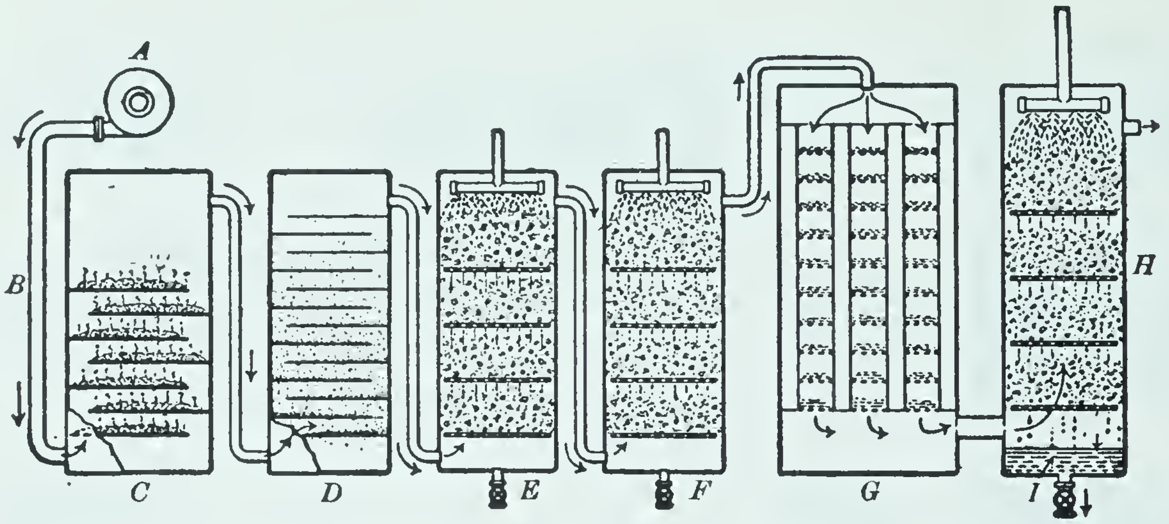


FIG. 256. Diagram to illustrate the commercial preparation of sulfuric acid by the contact process

The sulfur in the chamber *C* is burned by the air forced into the chamber by the blower *A*. The resulting sulfur dioxide and oxygen (air) are freed from dust by passing through the chambers *D* and *E*, and dried by a spray of sulfuric acid in *F*. The gases are then passed over the catalyst in *G*, where sulfur trioxide is formed by the union of the sulfur dioxide and oxygen. The resulting sulfur trioxide is absorbed in sulfuric acid sprayed from the top of the tower *H*, and the resulting product is drawn off at *I*

oxygen to form the acid, certain oxides of nitrogen being used as catalysts. The reactions are carried on in very large lead chambers into which oxides of nitrogen, sulfur dioxide, steam, and air are led in suitable proportions (Fig. 257).

How sulfuric acid acts. Sulfuric acid has a variety of properties which make it one of the most important of chemical substances.

1. *Action as an acid.* In dilute solution sulfuric acid acts as a very strong acid.

2. *Action as an oxidizing agent.* Sulfuric acid contains a large percentage of oxygen and, like nitric acid, is rather easily decomposed. So it is a very good oxidizing agent. When the concentrated acid is heated with sulfur or carbon or various other substances, it gives up oxygen, decomposing according to the equation

$$H_2SO_4 \longrightarrow H_2O + SO_2 + [O]$$

The symbol [O] means that the oxygen is not given off as gas but is used up in an oxidizing action:

$$H_2SO_4 + C \longrightarrow H_2O + SO_2\uparrow + CO\uparrow$$

A great quantity of concentrated sulfuric acid is used as an oxidizing agent in the manufacture of dyes, the sulfur dioxide which is formed being converted once more into sulfuric acid by the contact method.

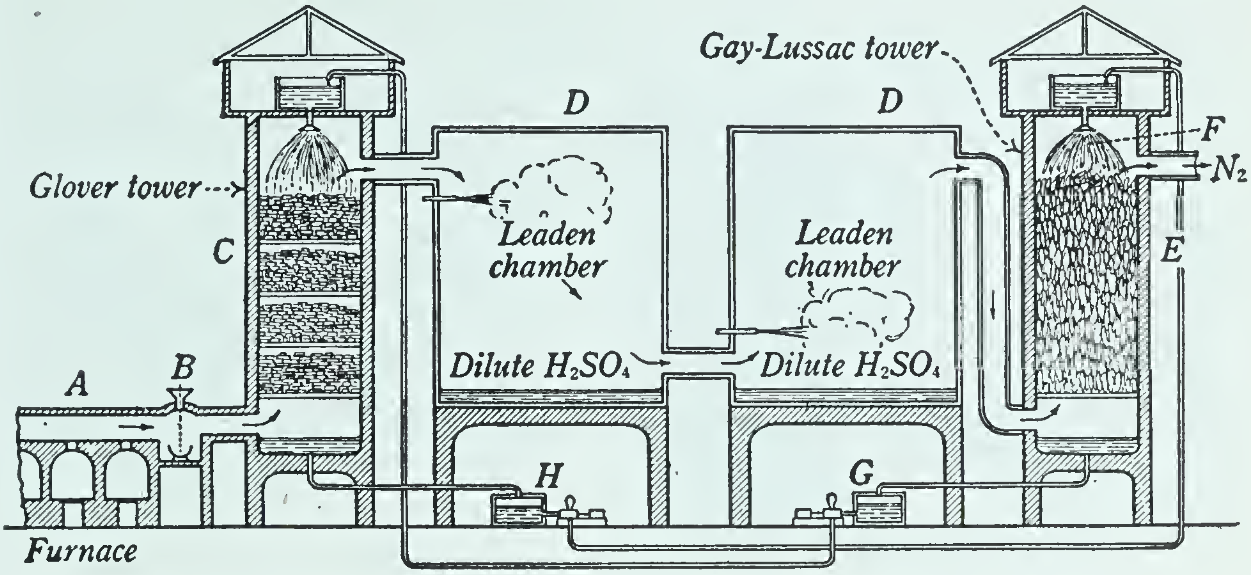


FIG. 257. Diagram to illustrate the preparation of sulfuric acid by the lead-chamber process

A mixture of sulfur dioxide (formed by burning sulfur or a sulfide in *A*), air (oxygen), and oxides of nitrogen (formed in *B* and *C*) passes through the tower *C* into the chambers *D*, *D*. Here the gases, together with steam forced into these chambers, react to form dilute sulfuric acid, which collects in the bottom of the chambers. The nitrogen of the air left after the oxygen is used in the reaction, together with nitrogen dioxide generated in the reaction, passes into the tower *E*, where they meet a spray of concentrated sulfuric acid, which dissolves the dioxide. The resulting solution is pumped back into the tower *C* and sprayed from the top, as shown in the figure. Trickling down the tower, it meets the incoming gases, which set free the dioxide gas so that it can be used over again. The acid made by this process is dilute, but has many uses (such as the manufacture of fertilizers)

3. ***Action on metals.*** *Dilute* sulfuric acid acts upon the metals above hydrogen in the electromotive series, forming salts of the acid (*sulfates*) and liberating hydrogen (p. 261). The *concentrated* acid, being a good oxidizing agent, first *oxidizes* nearly *any* metal to an oxide. The resulting oxide then reacts with more of the acid, forming a salt and water. For example, with copper the equations are

$$Cu + H_2SO_4 \longrightarrow CuO + H_2O + SO_2\uparrow \qquad (1)$$
$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O \qquad (2)$$

By canceling the formula of copper oxide in these equations (since the oxide produced in the first reaction is used up in the second) we may combine the two equations into a single one, namely,

$$Cu + 2\,H_2SO_4 \longrightarrow CuSO_4 + 2\,H_2O + SO_2\uparrow \qquad (3)$$

4. *Action on salts.* We have repeatedly seen that an acid of high boiling point, when heated with the salt of some acid of lower boiling point, will drive out the low-boiling acid (p. 314). The boiling point of sulfuric acid (338°) *is higher than that of almost any other common acid*; so it is largely used in the preparation of other acids. For example, the equation for the laboratory preparation of *nitric acid* is

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3\uparrow$$

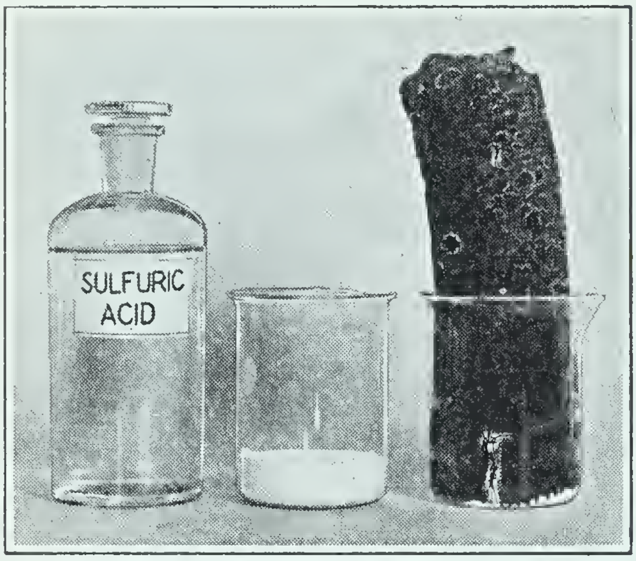


Fig. 258. The charring of sugar by sulfuric acid

The carbon set free forms a large honeycomb-like mass, owing to the escape of the steam formed in the reaction

5. *Action on water.* Concentrated sulfuric acid has a very great affinity for water and is an effective drying, or *dehydrating*, agent. Gases which have no chemical action upon sulfuric acid can be freed from water vapor by a process which consists of bubbling them through the concentrated acid.

Not only can sulfuric acid absorb water, but it will often take the elements hydrogen and oxygen away from some compound that contains them, decomposing the compound and combining with the water that is formed. It is for this reason that most organic substances, such as sugar, wood, cotton and woolen fiber, and even flesh, all of which contain considerable amounts of oxygen and hydrogen in addition to carbon, are charred by the action of the concentrated acid (Fig. 258).

Salts of sulfuric acid — sulfates. The sulfates form a very important class of salts, and many of them have commercial uses. Nearly all of them are soluble in water and, when found in nature, are usually in salt beds mixed with other soluble salts. This is true of the sulfates of sodium, potassium, magnesium, and calcium, which are also present in all sea water. Nearly all soluble salts are hydrated salts (p. 116)

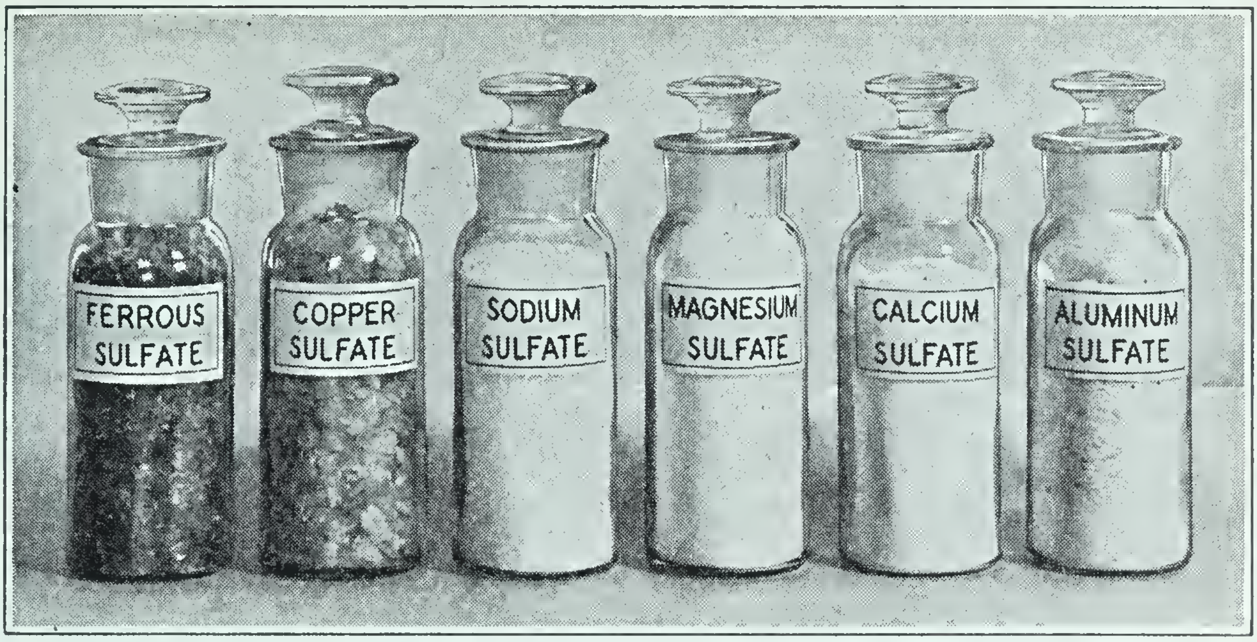


Fig. 259. A collection of common sulfates

and often have common names. The chief insoluble sulfates are those of lead, barium, and strontium; calcium sulfate is very sparingly soluble (Fig. 259).

Some important sulfates. The list of important sulfates includes the following:

Sodium sulfate, Na_2SO_4, used in making glass; Glauber's salt, $Na_2SO_4 \cdot 10\,H_2O$, used in medicine.
Potassium sulfate, K_2SO_4, used in making glass and as a fertilizer.
Magnesium sulfate, $MgSO_4$; Epsom salt, $MgSO_4 \cdot 7\,H_2O$, used as a drug.
Ferrous sulfate, $FeSO_4$; green vitriol, $FeSO_4 \cdot 7\,H_2O$, used in making ink and in purifying water.
Aluminum sulfate, $Al_2(SO_4)_3$. The hydrate, $Al_2(SO_4)_3 \cdot 18\,H_2O$ is used in water purification.
Copper sulfate, $CuSO_4$; blue vitriol, $CuSO_4 \cdot 5\,H_2O$, used in copperplating and in electrotyping, and in making various insecticides (Paris green, Bordeaux mixture).
Calcium sulfate, $CaSO_4$; gypsum, alabaster, $CaSO_4 \cdot 2\,H_2O$, used in making plaster of Paris.
Barium sulfate, $BaSO_4$ (barite), the mineral from which compounds of barium are made.

Test for sulfate ions, SO_4^{--}. Nearly all the *soluble* sulfates are freely ionized, as is sulfuric acid, giving sulfate ions, SO_4^{--}. Barium sulfate ($BaSO_4$) is one of the few sulfates *insoluble both in water and in acids.* So when a solution of a barium salt (such as barium chloride, $BaCl_2$) is added to a solution containing SO_4^{--} ions and hydrochloric acid, a *white precipitate* at once forms:

$$Ba^{++}, Cl^{-}_2 + H^{+}_2, SO_4^{--} \longrightarrow BaSO_4 \downarrow + 2\ H^{+}, Cl^{-}$$

This reaction gives us a delicate test for SO_4^{--} ions. There are other barium salts insoluble in *water*, but no others insoluble in *acids*; so hydrochloric acid must be added in making the test.

CHAPTER SUMMARY IN QUESTION FORM

1. (*a*) Write the names and formulas of two oxides of sulfur that are acid anhydrides; (*b*) also the names and formulas of the acids formed when these anhydrides combine with water.

2. Give two general methods for preparing sulfur dioxide, including equations for the reactions involved.

3. Write an accurate statement about sulfur dioxide by omitting the words in the following that do not accurately describe this compound:

Sulfur dioxide is a *gas* *solid* *liquid*. It has a *pleasant* *irritating* odor, and is *lighter* *heavier* than air. It is *easy* *difficult* to condense to the liquid state. It is an acid anhydride and combines with water to form *sulfurous* *sulfuric* acid.

4. Give three important chemical properties of sulfurous acid.

5. (*a*) What are salts of sulfurous acid called? (*b*) What gas is given off when these salts are treated with hydrochloric acid?

6. (*a*) Write the equation for the preparation of calcium bisulfite. (*b*) What important use has this compound?

7. Contrast the properties of sulfur dioxide and sulfur trioxide.

8. (*a*) Why is sulfuric acid sometimes called "the king of chemicals"? (*b*) Mention some of the important uses of this compound.

9. Describe the two common ways of making sulfuric acid, giving the advantages of each.

10. The following words apply to the preparation of sulfuric acid. Write a paragraph about the preparation of the acid, including these words:

sulfur sulfur dioxide catalyst water contact

11. (*a*) Is sulfuric acid a reducing or an oxidizing agent? (*b*) Give an example of its action.

12. (*a*) In general, what metals dissolve in dilute sulfuric acid? (*b*) What gas is evolved? (*c*) What becomes of the metal?

13. If a metal dissolves in concentrated sulfuric acid, (*a*) what gas is evolved? (*b*) what becomes of the metal?

14. (*a*) What is the action of sulfuric acid on salts? Illustrate your answer by writing the equation for the reaction of the acid (*b*) on sodium nitrate; (*c*) on sodium chloride.

15. (*a*) What name do we give a compound that has a strong affinity for water? (*b*) Is sulfuric acid such a compound?

16. (*a*) What name do we give to the salts of sulfuric acid? (*b*) Give the names and formulas of six of them.

17. (*a*) What compounds in water solution give the SO_4^{--} ion? (*b*) Give the test for this ion.

THOUGHT QUESTIONS

1. (*a*) Name three compounds studied that act as bleaching agents. (*b*) Name the conduct of each that gives it the power of bleaching.

2. In what ways do sulfur dioxide and carbon dioxide resemble each other?

3. Write the equation for the reaction that takes place when sulfuric acid is added (*a*) to Na_2CO_3; (*b*) to Na_2SO_3.

4. (*a*) Do the reactions in question 3 go to completion? (*b*) Why?

5. (*a*) Compare the reactions of nitric acid and of concentrated sulfuric acid on copper. (*b*) In what way do these reactions resemble each other?

6. Suggest a test for sulfites (not an ion test). (Recall that sulfur dioxide has a characteristic odor.)

7. Nitric acid is prepared by the action of sulfuric acid on sodium nitrate. Is the sulfuric acid used because it is a strong acid, because it has a high boiling point, because it is a liquid, or because it is a very cheap acid?

8. What precaution must one take when diluting concentrated sulfuric acid with water?

9. Do you think you could prepare nitric acid by treating sodium nitrate with hydrochloric acid?

10. State (*a*) the names and formulas of the three important acids studied; (*b*) their action on bases; (*c*) which of them can act as oxidizing agents; (*d*) which is a dehydrating agent?

11. In burning sulfur what relation exists between the volume of oxygen required and the volume of sulfur dioxide formed?

12. Calculate the percentage of oxygen in each of the oxides of sulfur.

13. Classify each of the following acids as monobasic, dibasic, or tribasic; also each of the salts as a normal or acid salt: HCl, KCl, H_2SO_4, $Ca(NO_3)_2$, H_2CO_3, $NaHCO_3$, H_3PO_4, Na_2HPO_4, H_2S, Ag_2S, NaHS.

OPTIONAL EXERCISES

1. Enumerate the reactions so far studied in which catalysts have been employed.

2. The ordinary concentrated sulfuric acid of commerce contains 98 per cent of hydrogen sulfate. A plant for the production of this acid consumes 100 tons of sulfur daily. What weight of the acid will be prepared daily, assuming that no sulfur is lost in the process (in other words, that a 100 per cent yield is obtained)?

CHAPTER XXXII

The Nitrogen Family

[A Typical Family Whose Members Show a Regular Gradation of Properties]

	Atomic Weight	Electrons in Orbits	Density of Solid	Compounds with Hydrogen and Oxygen
Nitrogen (N) . .	14.008	2:5	1.026	Strong acids
Phosphorus (P)	31.02	2:8:5	1.82	Less strong acids
Arsenic (As) . .	74.91	2:8:18:5	5.7	Weak acids
Antimony (Sb) .	121.76	2:8:18:18:5	6.684	Weak acids and bases
Bismuth (Bi) .	209.00	2:8:18:32:18:5	9.80	Base

Another family. We have studied the chlorine family and the sulfur family in the periodic arrangement of the elements (p. 323). We shall now learn something of the important members of a third family, namely, the nitrogen family.

The members of this family, as well as some of their properties, are shown in the table. It will be noticed that they have a regular gradation of properties. Nitrogen is a gas, while the others are solids whose densities increase with their atomic weights. Their acid-forming properties are in the reverse order. Nitrogen forms strong acids; antimony is on the border line between the metals and nonmetals, forming weak acids as well as weak bases. Bismuth is almost wholly a metal in its chemistry.

Judging from appearance alone, no one would ever think of grouping these elements together in one family; but in their chemical conduct these five elements have much in common. We have already studied nitrogen, and so we need not consider it further.

I. PHOSPHORUS

Some interesting facts about phosphorus. When anyone mentions phosphorus, we are apt to think of matches and bones; for it is well known that phosphorus (or its compounds) is the substance that makes matches take fire, and that one of its compounds, calcium phosphate, is the chief mineral material in our bones. The element itself is not

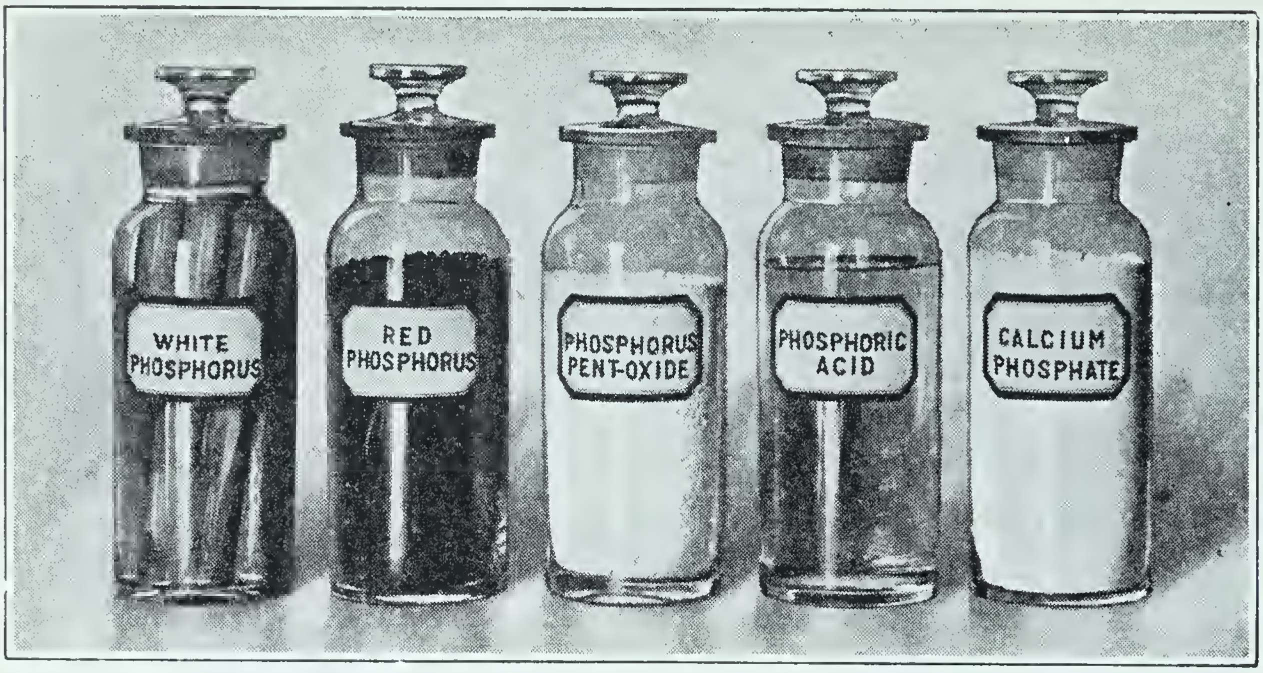


FIG. 260. Phosphorus and some of its most common compounds

easily made in the laboratory, so that it is rather remarkable that it has been known for such a long time. It was first prepared by the alchemist Brand, of Hamburg, in 1669. He got it by evaporating human urine to dryness, and heating the residue (which contained phosphates) with sand. He must have been greatly surprised to find that the substance he got in this way had such remarkable properties. It glowed in the dark, and took fire in the air, and burned with great vigor. So it was called *phosphorus*, or "light-bringer."

What is phosphorus like? Like many other elements, phosphorus occurs in a number of forms, of which the two most common are called (1) white phosphorus (although it is not white but slightly yellow) and (2) red phosphorus.

How do white and red phosphorus differ in properties? White phosphorus is a nearly colorless, translucent, waxy solid that melts at 44°. It is sold in the form of sticks covered with water to keep it from taking fire. Red phosphorus is a dark-red powder (Fig. 260).

White phosphorus is very poisonous, is easily soluble in carbon disulfide, and takes fire so readily that it must be handled with the greatest care. It is easily cut into pieces; but *this must always be done under water*, as otherwise the heat due to the friction of the knife blade will set the phosphorus on fire. Burning phosphorus in contact with the skin makes wounds that are very painful and slow in healing.

Red phosphorus has very different properties. It does not take fire easily, is not soluble in carbon disulfide, is not so poisonous, and has a high melting point. When it is distilled, and its vapor is suddenly chilled by passing it into cold water, it changes into white phosphorus. On standing at ordinary temperatures, the white phosphorus changes slowly into the red variety. The change is much more rapid in the presence of a catalyst, such as iodine.

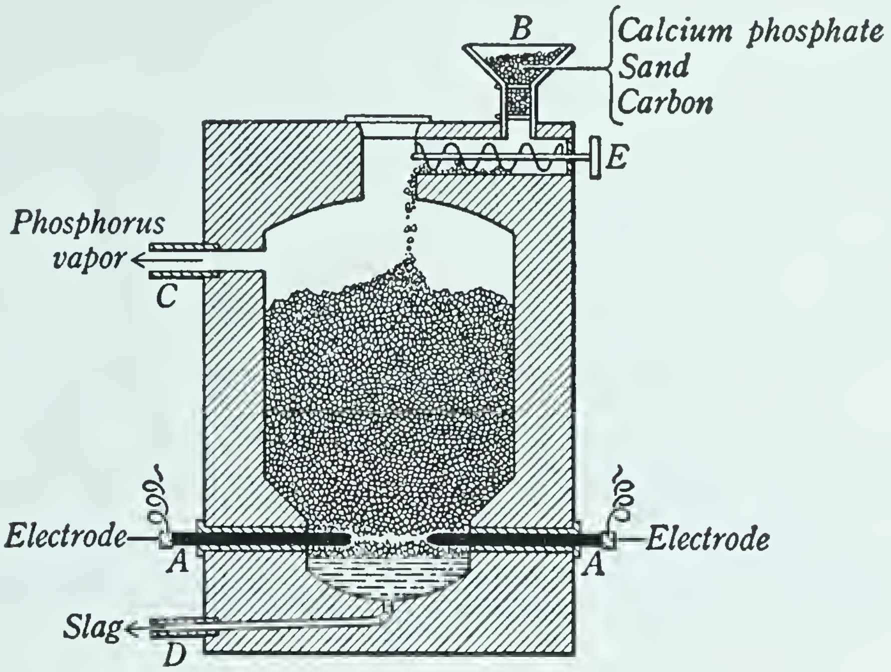


FIG. 261. The preparation of phosphorus

The raw materials used enter the furnace at *B* and are raised to a high temperature by the heat generated by the electric current passing between the electrodes *A*, *A*. The phosphorus is set free in the form of a vapor, passes out through *C*, and is condensed under cold water. The other products formed (slag) are drawn off at *D*

$$\text{Red phosphorus} \underset{\text{on long standing}}{\overset{\text{distilled and the vapor chilled}}{\rightleftarrows}} \text{White phosphorus}$$

How does phosphorus occur in nature? Its most common mineral form is calcium phosphate, $Ca_3(PO_4)_2$. The mineral *phosphorite* is impure calcium phosphate, while *apatite* consists of calcium phosphate combined with calcium fluoride or chloride. Calcium phosphate is the chief mineral in the bones of animals, and bone ash is largely this compound.

The preparation of phosphorus. Phosphorus is still prepared by the same general process (greatly improved, of course) that Brand used in its discovery. A mixture of calcium phosphate, sand, and carbon is heated in an electric

(Fig. 261) or fuel-fired furnace. The phosphate and sand react to set free the oxide, P_2O_5, which is then reduced by the carbon of the mixture. The resulting phosphorus vapor is condensed to a liquid under water and is then cast into solid stick form (Fig. 260).

The union of phosphorus with other elements. Phosphorus combines directly with many of the elements. Its most striking property is its affinity for oxygen, with which it unites to form the trioxide, P_2O_3, or the pentoxide, P_2O_5, according to the amount of oxygen at hand. The pentoxide is the more common of the two. It is a white, snowlike solid (Fig. 260) formed when phosphorus burns in plenty of air or oxygen. Its most marked property is its great affinity for water. For this reason, and also because it does not react with most gases, it is used as an effective drying agent for gases.

With chlorine, phosphorus forms the two chlorides PCl_3 and PCl_5, while with sulfur it forms a number of sulfides, the most important of which is the compound P_4S_3, called *phosphorus sesquisulfide.* This is a dark-colored solid and is used in making most kinds of matches.

The acids of phosphorus. The two oxides of phosphorus, P_2O_3 and P_2O_5, are both acid anhydrides (p. 304), uniting with water to make acids as follows:

$$P_2O_3 + 3\ H_2O \longrightarrow 2\ H_3PO_3 \text{ (phosphorous acid)}$$
$$P_2O_5 + 3\ H_2O \longrightarrow 2\ H_3PO_4 \text{ (phosphoric acid)}$$

In addition to these two there are some other acids of phosphorus, but of them all phosphoric acid is the most important. The pure compound can be got in colorless crystals; ordinarily the acid contains a little water, and it is then a thick, sirupy liquid (Fig. 260). It is prepared either by treating its most common salt, calcium phosphate, with sulfuric acid or by burning phosphorus vapor (formed in the preparation of phosphorus) in air and combining the resulting oxide (P_2O_5) with water, as shown in the above equation.

Salts of phosphoric acid — the phosphates. While phosphoric acid has only a limited (though increasing) use, its salts are of much interest. By far the most important of these is calcium phosphate, $Ca_3(PO_4)_2$, widely and abun-

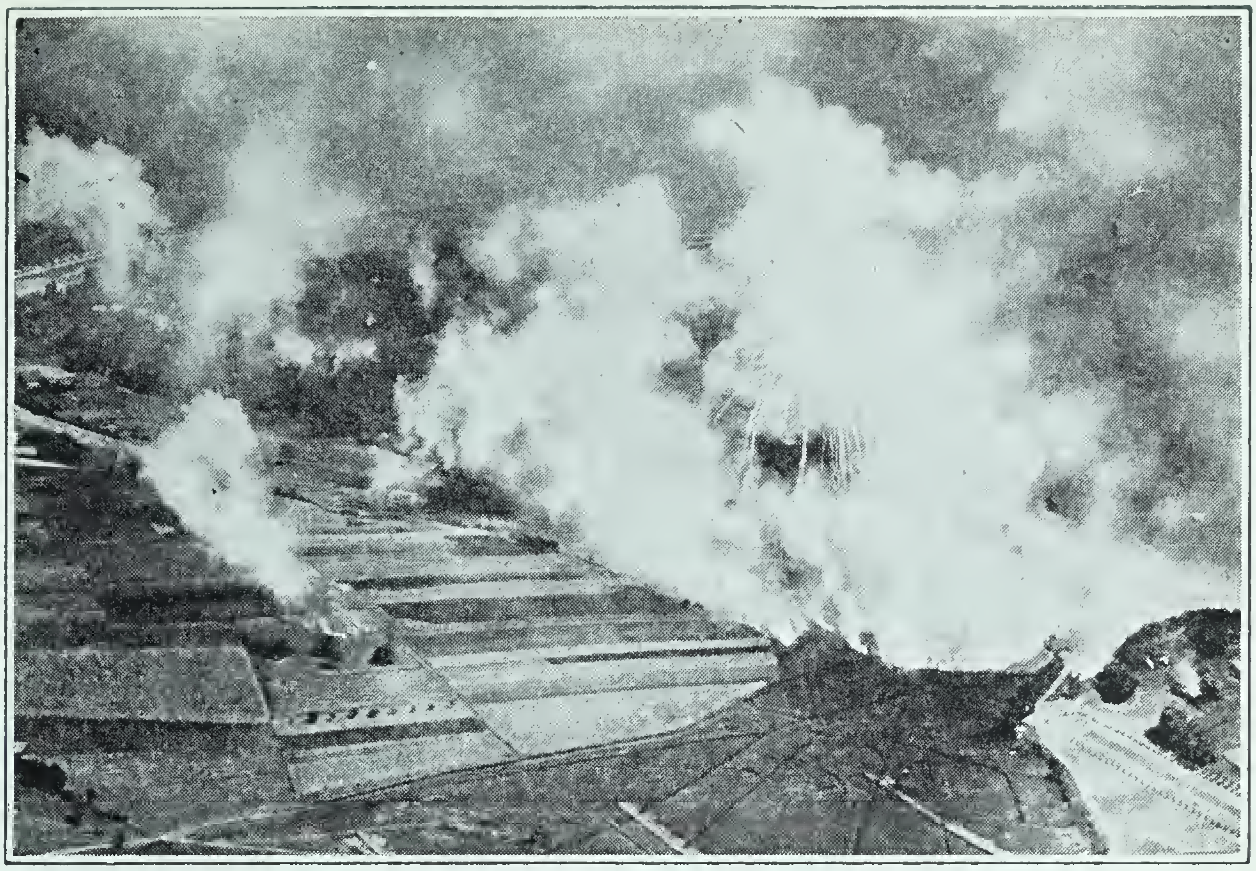


Fig. 262. The use of phosphorus in the World War to conceal troops

When troops were ready for an attack, shells filled with phosphorus were fired in advance of the lines. When these exploded, the phosphorus burned, forming dense clouds of the oxide, which entirely concealed the troops

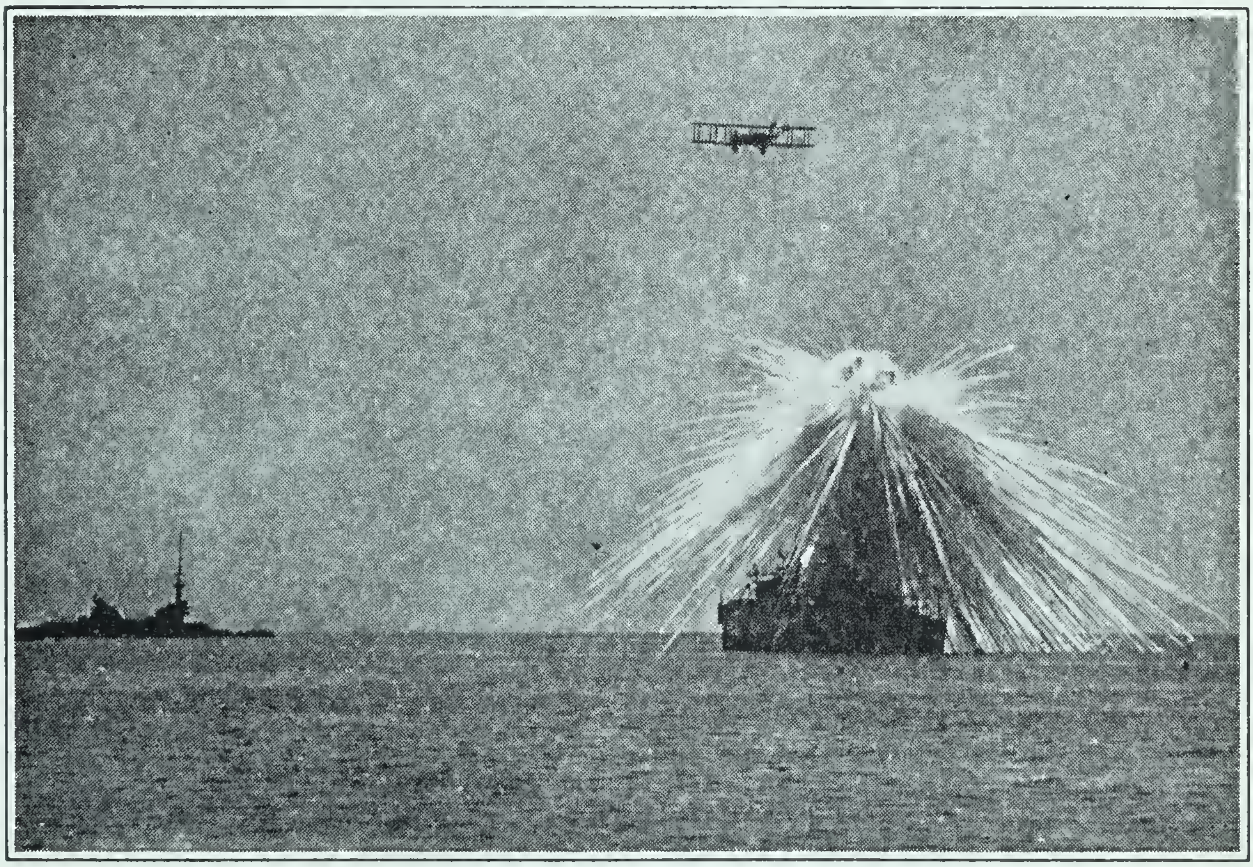


Fig. 263. The use of phosphorus in naval warfare

A phosphorus bomb may be dropped by an airplane upon a ship, enveloping it in a dense cloud, either to conceal its exact location or to make it impossible for it to fire accurately. The figure shows an airplane which has made a "hit" with a phosphorus bomb. (Photograph by United States Army Air Corps)

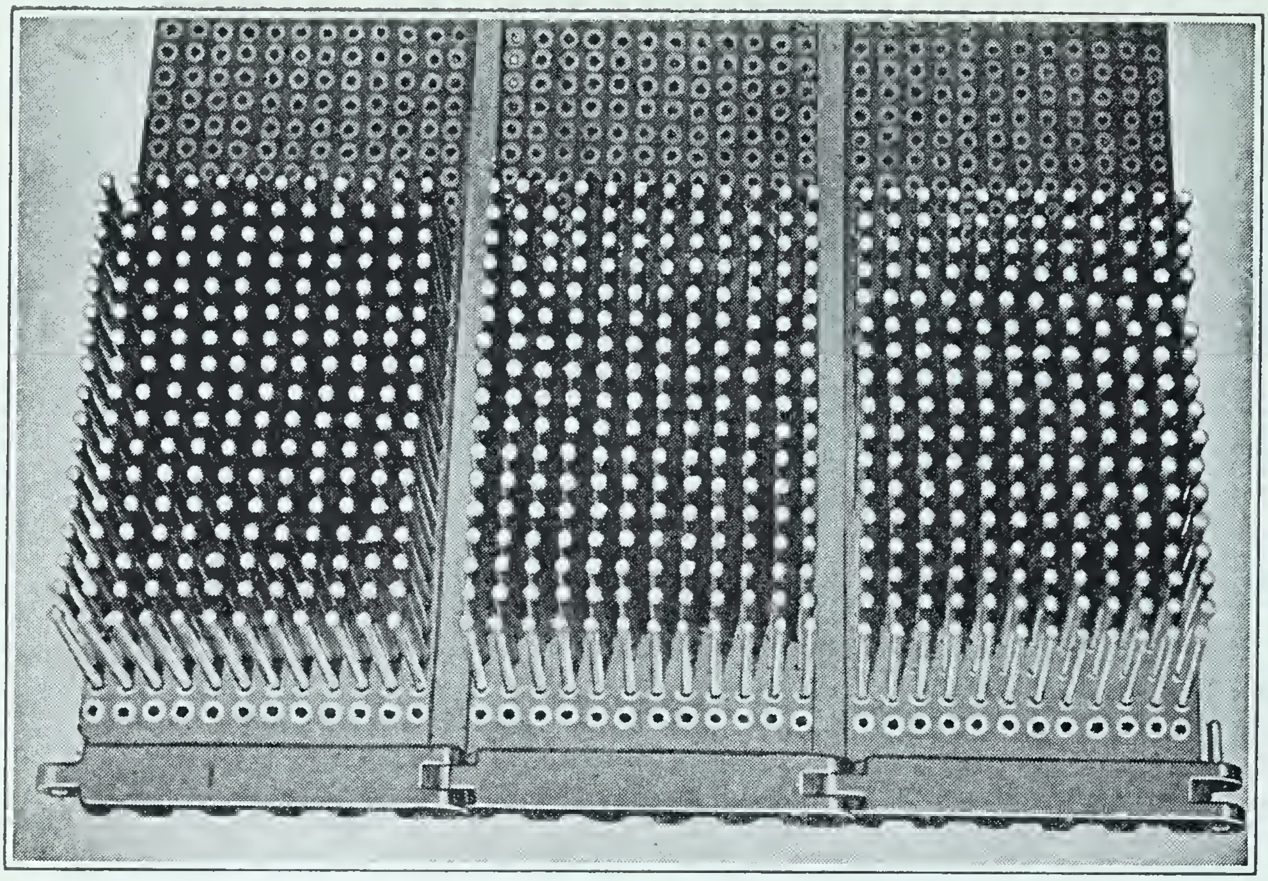


Fig. 264. Match sticks newly dipped

Three plates full of holes into which match sticks are inserted to keep them separated from each other while the free ends are dipped into the liquid preparation to form the match head

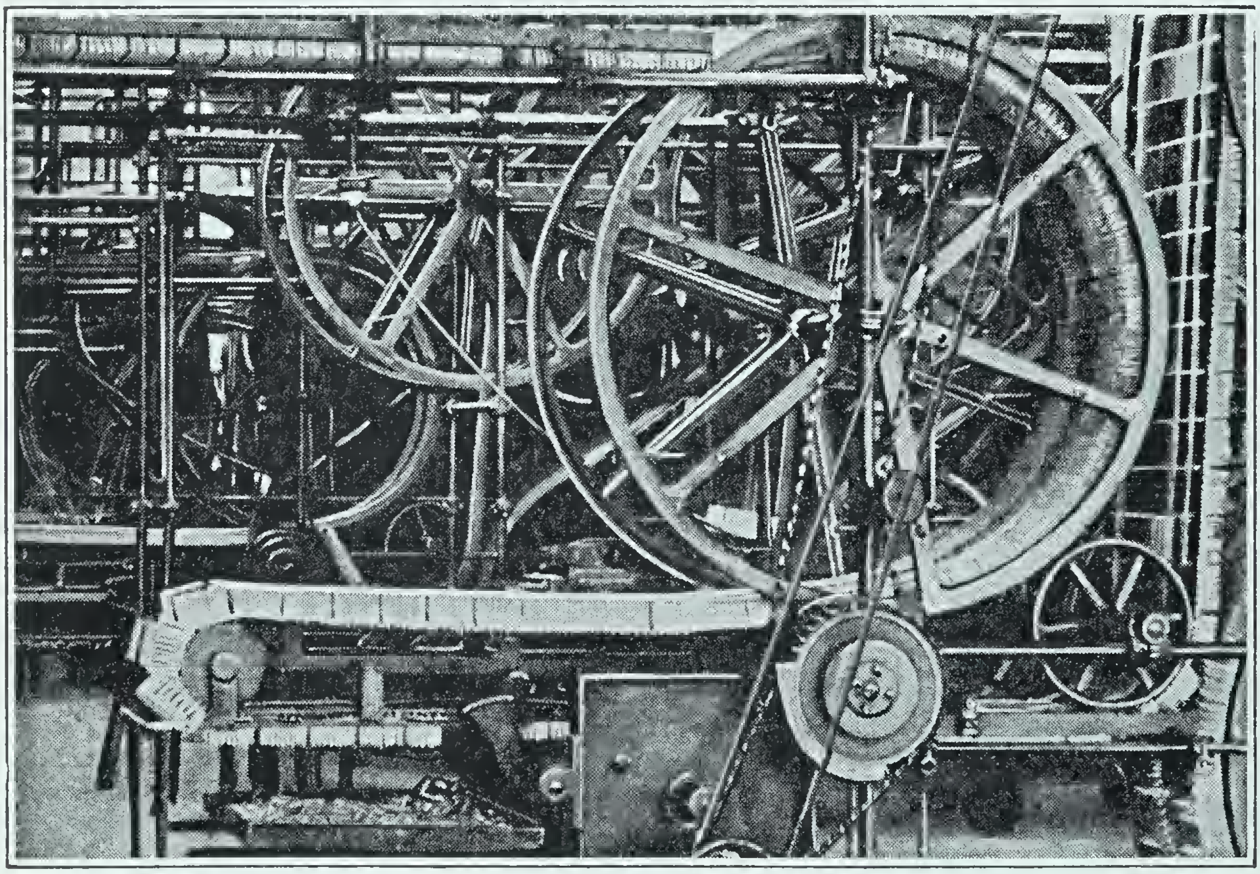


Fig. 265. Forming the match head by dipping the match stick

Plates full of match sticks (the same as shown in Fig. 264, but much reduced in size) are carried on an endless belt in such a way as to dip the free ends of the sticks successively into the preparations that form the bulb and tip, and then to dry the matches dantly distributed in nature and largely used in making fertilizers. As phosphoric acid is tribasic, it forms both acid and normal salts. Thus, the following sodium salts are known, in which 1, 2, and 3 hydrogen atoms, respectively, have been displaced by the corresponding number of sodium atoms:

H_3PO_4 . . .	phosphoric acid
NaH_2PO_4 . .	primary sodium phosphate, or monosodium-hydrogen phosphate
Na_2HPO_4 . .	secondary sodium phosphate, or disodium-hydrogen phosphate
Na_3PO_4 . . .	tertiary sodium phosphate, or trisodium phosphate

Some of these phosphates are used in baking powders, water-softeners, washing powders, tooth pastes, and dental cements.

The uses of phosphorus. Phosphorus is used in making some of its compounds as well as in the manufacture of special bronzes. During the World War large amounts were used to make *smoke clouds* by burning the element in the air. The resulting oxides formed dense clouds that could conceal troops and ships (Figs. 262 and 263). *The most important use of phosphorus is in making matches.*

Matches — millions of them made daily by a single machine. It has been said that the greatest discovery ever made was how to start a fire. Certainly one of the most useful of all inventions was an easy way to start a fire by the use of matches. Friction matches were first invented by John Walker of England, about 1826. These were very crude and were ignited by pulling them between folds of sandpaper. In the United States the first friction matches were made in 1836.

In all matches made today, ignition depends either on phosphorus or on one of its compounds. Formerly, white phosphorus was used; but this led to so many cases of poisoning that it was finally given up, and in its place either *red phosphorus* or *phosphorus sesquisulfide* (P_4S_3) is now used. At present we have two well-known kinds of matches — the "*strike-anywhere*" and the *safety* match.

The strike-anywhere matches. These are composed of the following parts:

(1) The *stick*, which is of soft pine wood dipped into a solution of ammonium phosphate (to give "nonglowing" properties) and then into melted paraffin. (2) The *bulb*, which is a mixture containing (*a*) an oxidizing agent, usually potassium chlorate; (*b*) some material easily oxidized, as sulfur or rosin; (*c*) some filling material like ground glass; and (*d*) a binding substance like glue, to hold the parts together. (3) The *tip*, made of the same materials used for the bulb, together with a large percentage of phosphorus sesquisulfide.

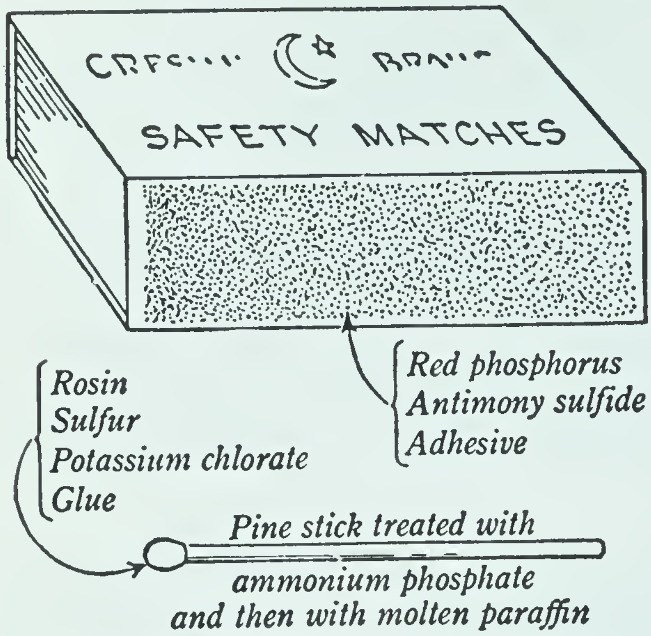


FIG. 266. The materials present in safety matches

When rubbed, the tip starts to burn. This, in turn, sets fire to the bulb, the combustion being supported by the oxidizing agent present. This larger flame ignites the paraffin on the stick and so, finally, the stick itself. Figs. 264 and 265 show some steps in the making of these matches.

Safety matches. These have the following parts:

(1) The *stick*, as in the strike-anywhere matches. (2) The *bulb*, made up of a mixture of potassium chlorate, rosin, sulfur, and glue to hold the constituents together. (3) *The mixture on the side of the container.* This is made up of red phosphorus, antimony sulfide (Sb_2S_3) or iron sulfide (FeS_2), and a glue to make the mixture stick to the side of the box (Fig. 266). Since the bulb contains no phosphorus, it will not take fire unless drawn over the red phosphorus mixture on the side of the box.

II. ARSENIC

Where is arsenic found and what is it like? When we hear the word *arsenic* we are apt to think of a poison, because everyone knows that materials which contain arsenic are poisonous. Like phosphorus the element arsenic can take a number of forms, the usual one being a steel-gray solid. In nature it is found combined with sulfur as a bright-red or yellow mineral. Small percentages, combined with metals, are present in certain ores of copper. In getting copper from these ores the oxide of arsenic As_2O_3 is obtained as a by-product. A few years ago it was regarded as a nuisance by the copper-smelters, but it is now in large demand in the manufacture of insecticides.

The element arsenic can be obtained from the oxide by heating with carbon:

$$2\,As_2O_3 + 3\,C \longrightarrow As_4 + 3\,CO_2$$

It burns when heated in air, forming the oxide As_2O_3.

Some important compounds. When hydrogen is set free from acids in contact with arsenic or with its compounds, a *very poisonous*, colorless gas known as *arsine* (AsH_3) is formed. The most familiar compound of arsenic is the oxide As_2O_3, known as arsenic trioxide or *arsenious oxide* or often as *white arsenic*. Ordinarily it is referred to simply as *arsenic*. It is a rather heavy white solid, sold either as a crystalline powder or in lumps resembling porcelain in appearance. It is very poisonous.

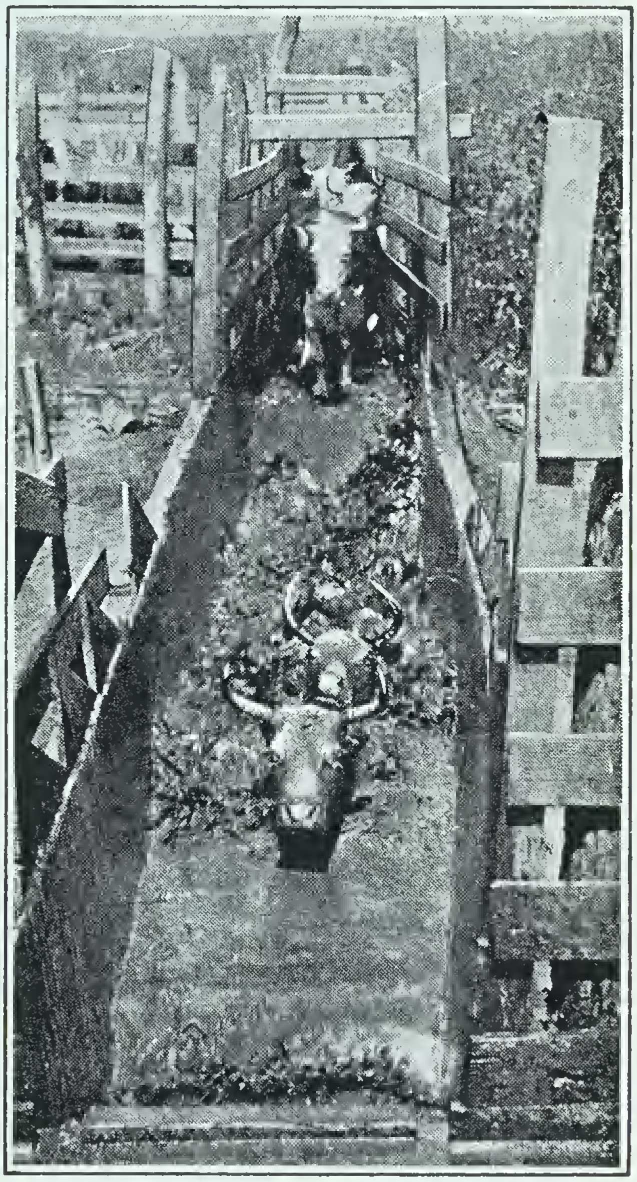


FIG. 267. Cattle being driven through a solution of arsenic compounds

These compounds kill any parasites infesting the animals

Arsenic also forms a number of acids, the most important of which are *arsenious acid* (H_3AsO_3) and *arsenic acid* (H_3AsO_4). It will be noticed that the formulas of these acids are like the formulas of the corresponding acids of phosphorus. The salts of these acids have many uses.

Uses. Arsenic in the free state is little used. About 0.5 per cent of arsenic is added to lead used in making shot, because this makes the lead harder and the shot rounder. The oxide As_2O_3 is used in making all the other compounds of arsenic. It is also used in making glass and as a preservative in mounting the skins of birds and animals. Its greatest uses are in the manufacture of weed-killers and of insecticides for spraying trees, vegetables, and cotton crops and killing parasites on stock (Fig. 267).

Arsenic insecticides. Several compounds of arsenic have important uses as insecticides. *Paris green* and *Scheele's green* are salts made by treating solutions of copper salts with arsenious oxide. The commercial *lead arsenate*, so widely used as a spray (as in Fig. 246), is chiefly $Pb_3(AsO_4)_2$, and calcium arsenate is the corresponding calcium salt.

III. ANTIMONY

A brief description. Antimony is a silverlike, brittle, crystalline solid a little lighter than iron. It melts at 630.5° and expands somewhat on solidifying. It is found in nature principally as *stibnite* (Sb_2S_3), and the world's supply comes largely from China. It is obtained by heating melted stibnite with iron:

$$Sb_2S_3 + 3\ Fe \longrightarrow 2\ Sb + 3\ FeS$$

It forms a number of compounds which resemble the corresponding compounds of arsenic in composition and properties. Its chief use is in making *alloys* (Chap. XLI), especially the ones known as *type metal* and *Babbitt metal.*

IV. BISMUTH

Its looks and its uses. Bismuth has the general properties of a metal, and in appearance differs from antimony chiefly in having a slightly rosy tint. It is found in nature in the free state as well as in various compounds, and our supply comes chiefly from Peru and Bolivia. It has a low melting point (271°), and its chief use is in the making of alloys which melt at a low temperature (Fig. 268).

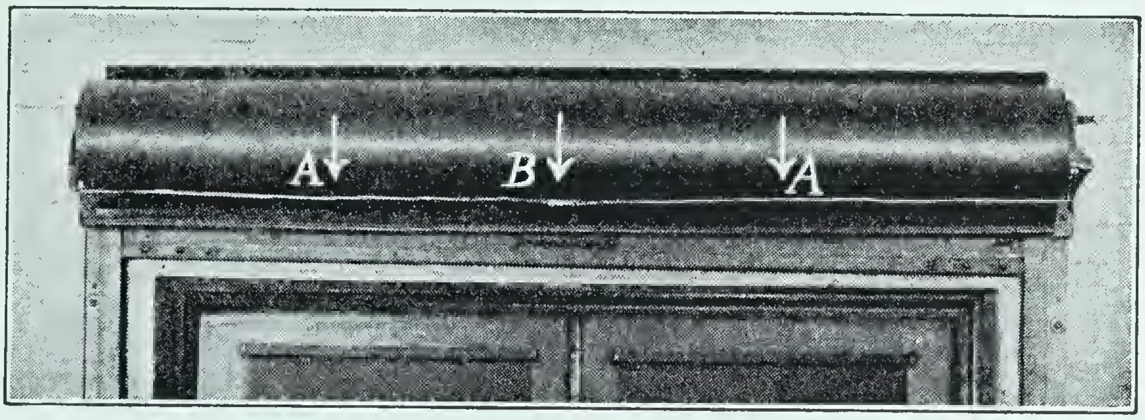


FIG. 268. An automatic fire curtain above a door

The fire curtain is held in place by the wires *A*, *A*, which are united at *B* by a link of low-melting alloy. When a fire melts the alloy union, the wires are released and the curtain drops

Bismuth not only looks but acts like a metal, forming salts such as the chloride, $BiCl_3$, and the nitrate, $Bi(NO_3)_3$. These salts react with water as shown in the following equations:

$$BiCl_3 + H_2O \rightleftharpoons BiOCl \downarrow + 2\ HCl$$
$$Bi(NO_3)_3 + H_2O \rightleftharpoons BiONO_3 \downarrow + 2\ HNO_3$$

The compound BiOCl, called *bismuth oxychloride*, and the corresponding *bismuth oxynitrate*, $BiONO_3$, are white solids, the latter having important uses in medicine.

CHAPTER SUMMARY IN QUESTION FORM

1. Name the two chief forms of phosphorus.

2. Which form of phosphorus is (*a*) the more active? (*b*) the more stable?

3. How can (*a*) white phosphorus be converted into red phosphorus and (*b*) the red into the white form?

4. What precautions must we take when working with white phosphorus?

5. Give the chemical name and formula of the compound from which phosphorus is obtained commercially.

6. Give the most striking property of white phosphorus.

7. (*a*) Give the formulas and names of two oxides of phosphorus. (*b*) Are they acid anhydrides? (*c*) What relation do they bear to acids? (*d*) What are the names and formulas for the acids formed when they react with water?

8. What name do we give to an acid, like phosphoric acid, that has three replaceable hydrogen atoms?

9. (*a*) Give the names and formulas for the salts which phosphoric acid forms with sodium. (*b*) Indicate which are normal and which are acid salts.

10. What compound of phosphorus is mined in large quantities for use as a fertilizer?

11. What is the chief use of phosphorus?

12. (*a*) What materials are present in the bulb of the match head of the "strike-anywhere" matches? (*b*) in the tip?

13. (*a*) What materials are present in the bulb of the match stick of the safety match? (*b*) on the side of the box?

14. (*a*) Name three compounds of arsenic of commercial importance. (*b*) For what is each used?

15. What are the chief uses of antimony and bismuth?

THOUGHT QUESTIONS

1. What name would you give to the two forms of phosphorus?

2. Mention two properties of white phosphorus that one should be careful to keep in mind when working with it.

3. What elements so far studied occur in allotropic forms?

4. (*a*) What is the approximate weight of phosphorus in your body (p. 30)? (*b*) In what form is it present?

5. Give the function of each of the materials used in making matches.

6. Give reasons for keeping (*a*) sodium in kerosene, (*b*) phosphorus in water, (*c*) ammonia in rubber-stoppered bottles, and (*d*) hydrofluoric acid in wax bottles.

7. Write the equations for the reactions that occur in the following cases: (*a*) phosphorus burned in air; (*b*) phosphorus pentoxide and water; (*c*) bismuth chloride and water.

OPTIONAL EXERCISES

1. (*a*) What weight of phosphorus can be obtained from 50 kg of pure calcium phosphate? (*b*) What weight of pure phosphoric acid?

2. Type metal contains about 18 per cent of antimony. What weight of stibnite would be required to furnish the antimony for making 100 lb of type metal?

CHAPTER XXXIII

Soils, the Source of All Our Food Supply; Fertilizers

[What Soils Are and What They Must Contain]

The importance of soils and fertilizers. Unless we are interested in growing crops or vegetation of some kind, we give little thought to the soil. It is common and abundant, and we take it for granted. To realize its great importance we have only to try to name some food that does not come either directly or indirectly from the soil.

In the early days of our country there was little trouble in growing crops, because the soil was rich in the food material necessary to the growth of the plant. As time passed and one crop followed another, the soil's supply of such food material slowly diminished, and new stocks had to be added as *fertilizer*. The extent to which this has had to be done is shown by the fact that today the manufacture of fertilizers is one of our largest industries.

So important is the character of the soil to the welfare of the people that the Federal and state governments have established agricultural experiment stations in the different states (Fig. 269); and these, together with the colleges of agriculture, are trying to solve the mysteries of the soil. Farmers send in samples of "sick" soils, to have their troubles diagnosed and cures recommended, much as we go to the physician with our bodily ills. In an elementary text we can learn only a few facts in reference to soils, but these are of importance and may help to arouse interest in this subject of national importance.

How there came to be soils. Soils result from the breaking down of rocks into small pieces or powder. Many agencies contribute to this change, prominent among them being the action of water and air. The glaciers which at times have covered large portions of the globe had a very powerful grinding effect, breaking off large boulders and gradually grinding them to a powder.

Fig. 269. One of the fields of the Ohio Agricultural Experiment Station

The picture shows a number of small plots of ground where soy beans and various grains are being grown under different conditions

Water helps in a number of ways. It finds its way into cracks and crevices, and on freezing it expands and so cracks the rocks. It dissolves out certain rock materials so that the remainder of the rock tends to crumble. Running water carrying sand and gravel in suspension grinds the rocks with which it comes in contact.

Air also acts upon some rocks chemically, while strong winds carrying sand dust have a powerful sandblast effect. When plants get a foothold, they help greatly, not only by the mechanical action of their roots but also through the chemical action of the various products formed in their decay. The soil is the result of all these agencies acting through long periods of time.

Different kinds of soil. Since the rocks in different places vary widely in composition, the resulting soils will vary in a corresponding way. So we have limestone soil, made chiefly by the weathering of limestone; and sandy and clay soils, which are richer in silicates. When plants decay, certain acid products are formed, so that soils tend to become acid. Most crops do not thrive on such soil. If the soil contains limestone, the acids will be neutralized as fast as they are formed, and the soil will be kept *sweet*. If the soil does not contain limestone, then ground limestone, or calcium hydroxide (hydrated lime), should be added (Fig. 270).

Soils differ not only in composition but also in their physical properties. Some soils are light and easily allow water and air to circulate through them — conditions that are essential to a fertile soil. Others are compact and nearly water-tight. Crops do not thrive on wet soils; and such soils must be freed from excess water by drainage.

Plant food and fertilizers. With the exception of carbon dioxide (and possibly a little oxygen) absorbed from the air, the growing plant gets its nourishment from the soil. So the soil must contain an adequate supply of suitable plant food, and this, in addition to water, includes both mineral matter and organic matter (*humus*). Since this supply is continually being drawn upon by the growing plant, it is necessary to renew it by fertilizers (Figs. 271, 272).

What foods do plants need? While different plants need somewhat different foods, yet experiments have shown that in general a soil that has the necessary physical properties may be kept fertile by adding four different substances as follows: (1) nitrogen compounds, (2) phosphates of calcium, (3) sulfur compounds, and (4) potassium compounds. Of course, all these compounds must be soluble and of such a nature that the plants can use them.

In addition to the elements present in the compounds just named, recent experiments indicate that small percentages of some other elements are required. These are iron, manganese, zinc, copper, silicon, chlorine, aluminum, and boron. Since the percentage of these required is very small, it is probable that most soils contain the necessary supply. If not, compounds of these elements must be supplied in a form which the plants can use.

Sources of the constituents of fertilizers. The commercial sources of each of the ordinary constituents of fertilizers are as follows:

1. ***Nitrogen compounds.*** Sodium nitrate, ammonium sulfate, cyanamide (p. 535), and urea (p. 454) are all used; also nitrogenous organic matter such as dried blood and waste from slaughter houses, fish scraps, and animal manures.

2. ***Phosphates.*** Ground bones are especially valuable, since they contain some nitrogen in addition to calcium

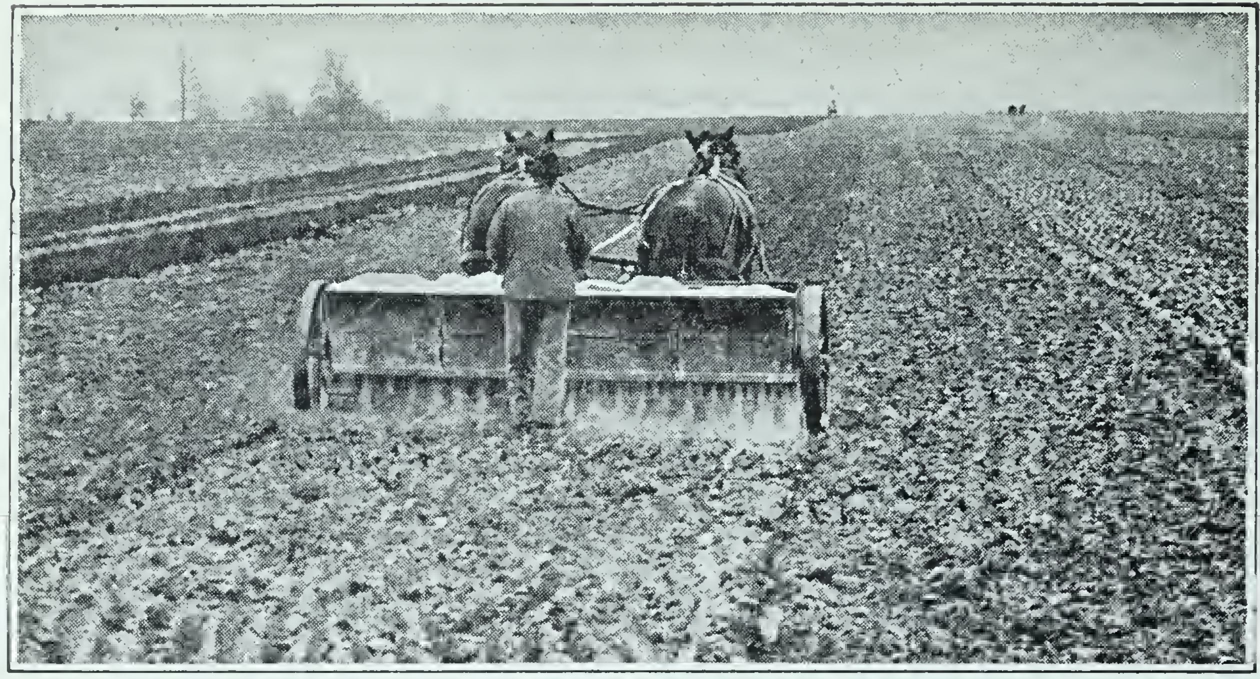
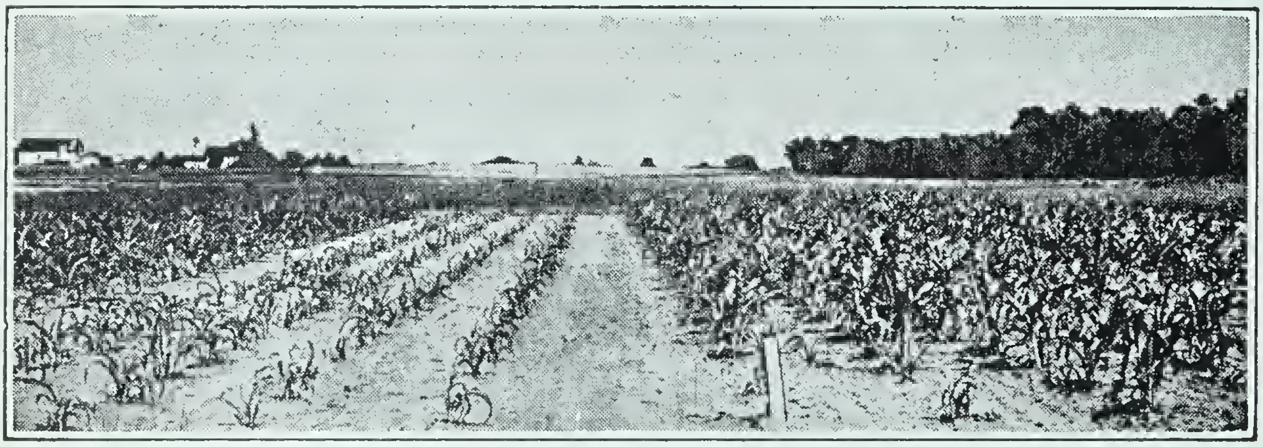


FIG. 270. Acid soil being treated with either calcium hydroxide (hydrated lime) or ground limestone to neutralize the acid



Nonfertilized soil   Fertilized soil

FIG. 271. A view of a cornfield, showing the effect of fertilizers

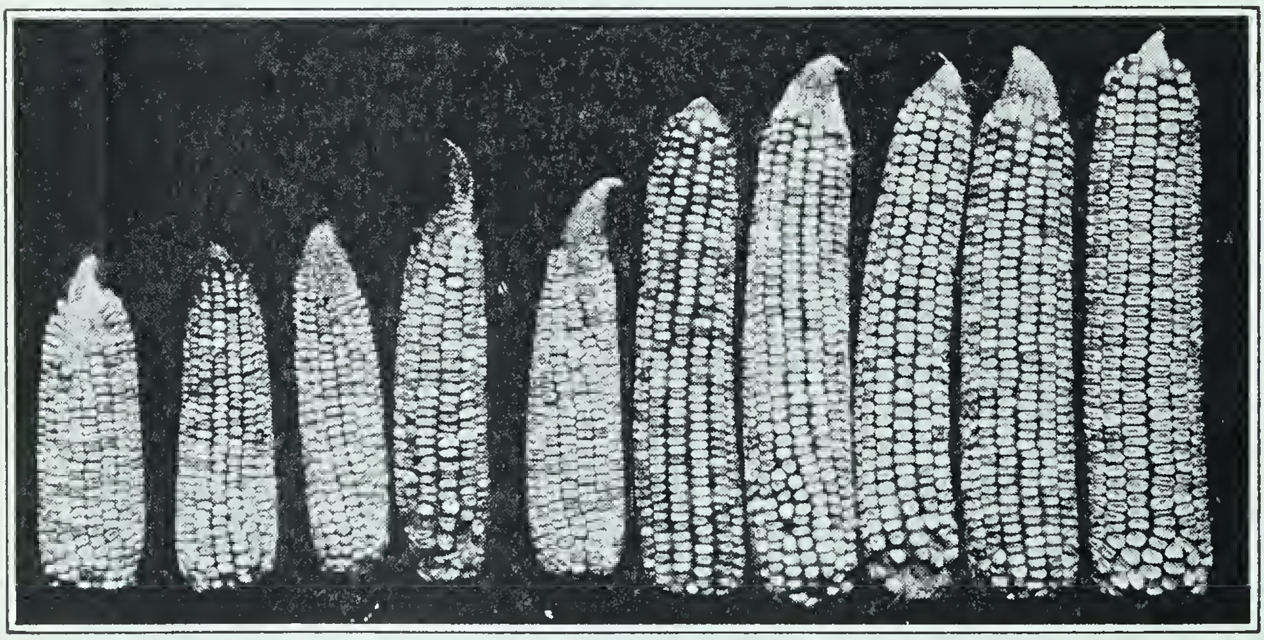


FIG. 272. Effect of fertilizers in growing corn

The five small ears were the average of those grown on the nonfertilized soil shown in Fig. 271: the five large ears were the average of those grown on the fertilized soil

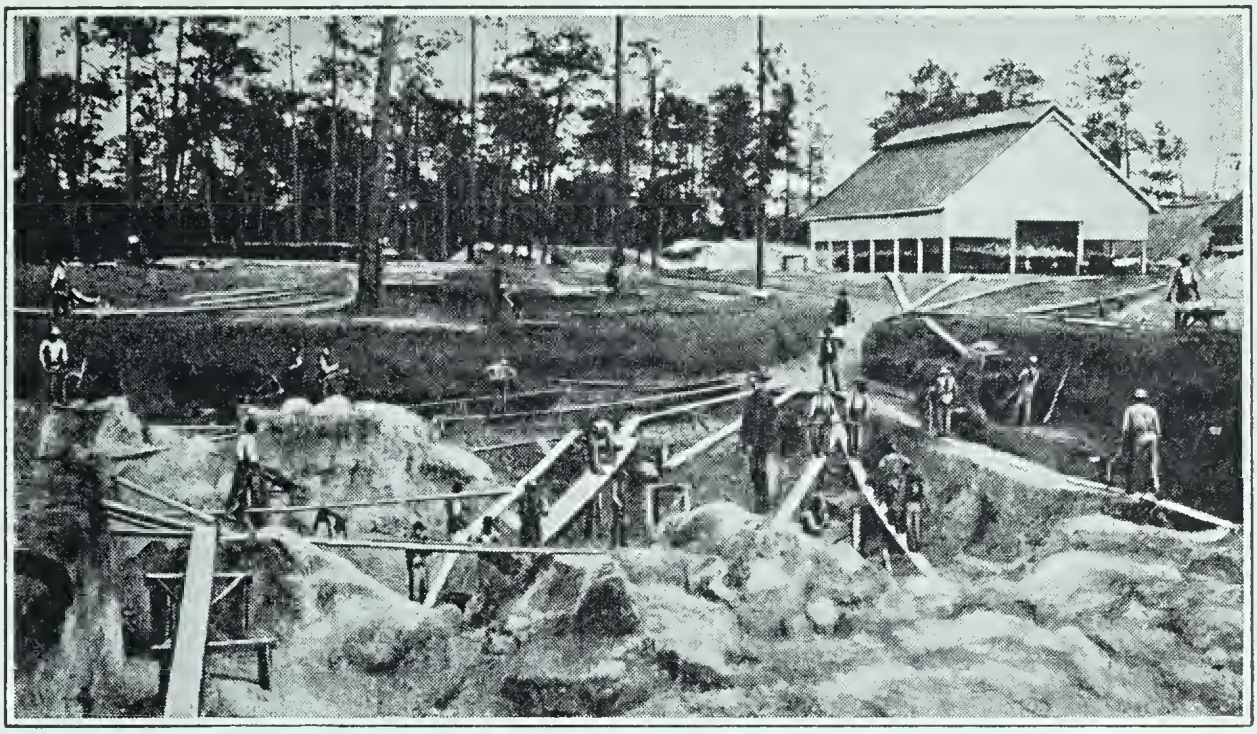


FIG. 273. Mining phosphate rock in Florida for use in the manufacture of fertilizers

phosphate. But this is a very limited source, and the great supply comes from the rock phosphates, which contain about 70 per cent of calcium phosphate. These rock phosphates are found in many places throughout the United States. The largest deposits are in Florida and Tennessee, where several million tons are mined each year (Fig. 273).

But calcium phosphate is insoluble, and if used as a fertilizer it must first be changed into a soluble form so that the plants can take it up. This is done by treating the rock with sulfuric acid. In this way the insoluble calcium phosphate is converted into a soluble acid phosphate, $Ca(H_2PO_4)_2$:

$$Ca_3(PO_4)_2 + 2\,H_2SO_4 \longrightarrow 2\,CaSO_4 + Ca(H_2PO_4)_2$$

Phosphoric acid is sometimes used in place of sulfuric acid to form the acid phosphate, in order that a fertilizer that is richer in phosphorus may be obtained.

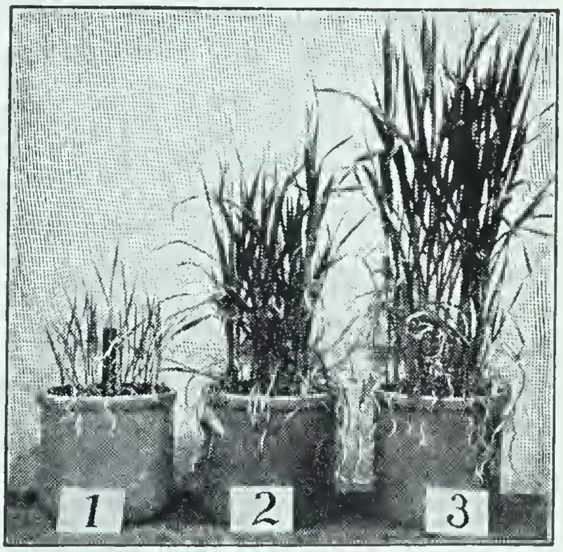
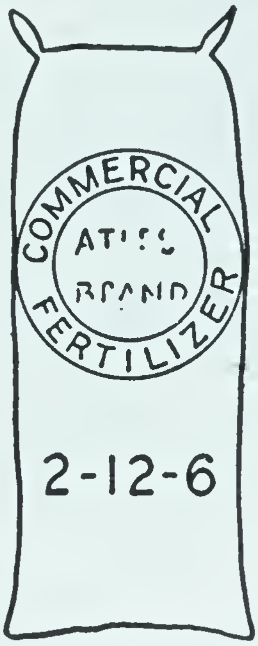


FIG. 274. The effect of different fertilizers on the growth of the same plants

3. ***Sulfur compounds.*** It will be seen from the equation just given that calcium sulfate is formed along with the cal-

cium acid phosphate, so that the product is a mixture of these two compounds. It was long thought that the value of the fertilizer depended entirely upon the phosphate. Now we know that the calcium sulfate adds to the value of the fertilizer, furnishing sulfur and improving the physical qualities of the soil.



The first of the three figures stamped on the bag gives the percentage of nitrogen, the second the percentage of phosphorus (calculated as P_2O_5), and the third the percentage of potassium (calculated as K_2O)

Fig. 275. A bag of fertilizer

4. ***Potassium compounds.*** For many years practically all the potassium compounds used in the United States came from Germany and France, where large deposits occur. In recent years new supplies have been found in New Mexico, in Texas, and, to a less extent, in Searles Lake, California, so that the United States now obtains from within its own borders a large percentage of the potassium compounds used in its fertilizer industry.

Commercial fertilizers. As a rule the fertilizers on the market are mixtures of the four fundamental materials mentioned above. The composition is varied to suit the crop to be grown as well as the nature and condition of the soil. For example, potatoes demand a fertilizer rich in potassium, while a cereal, such as wheat, is benefited more by one rich in phosphates. Instead of using a fertilizer containing all four constituents, it is better to find out by experiment (Fig. 274) just what plant food is lacking in a given soil and then to make a mixture of fertilizing materials such as will meet its needs. Fig. 275 shows the usual way of marking the packages of fertilizers sold on the market.

CHAPTER SUMMARY IN QUESTION FORM

1. What relation does soil bear to rock?

2. Name four agencies that help to make soil.

3. Give examples of two kinds of soil.

4. What word means "the organic portion of soil"?

5. Name four substances which will maintain the fertility of soils that have the necessary physical properties.

6. Name three chemical compounds which may be added to soil to keep up a supply of nitrogen for growing plants.

7. Name three sources of phosphates.

8. Should you say calcium phosphate is soluble, very soluble, nearly insoluble, or insoluble?

9. Name two compounds, valuable as fertilizers, that result from the action of sulfuric acid on calcium phosphate.

10. Name four elements that are made available to plants by adding to the soil a complete fertilizer.

THOUGHT QUESTIONS

1. Why do farmers add calcium hydroxide (hydrated lime) to clay soils?

2. How can we tell the kind of fertilizer that any given soil requires?

3. What are the sources of the sodium nitrate and ammonium sulfate used in fertilizers?

4. (*a*) Have you ever seen any evidence that the roots of plants and trees exert strong mechanical pressure? (*b*) If so, give examples.

5. (*a*) What kind of crops enrich the soil? (*b*) How do they accomplish this?

6. Ground bones are sometimes used as fertilizers, but their action is slow. Explain.

7. How could you find out what mineral products are withdrawn from the soil by different kinds of crops?

OPTIONAL EXERCISES

1. Calculate the percentage of phosphorus in pure calcium phosphate.

2. In a certain fertilizer plant 50 tons of rock phosphate are used daily. The rock phosphate contains 80 per cent of calcium phosphate. The sulfuric acid used contains about 50 per cent of hydrogen sulfate. What weight of this acid will be necessary to change the phosphate present in the rock into the soluble acid phosphate?

UNIT READINGS

BEERY. *Stuff.* [Chapter VII, "The Safety Match," tells an interesting story.]

CLARKE. *Marvels of Modern Chemistry.* [Chapter XIV tells of sulfur; Chapter XV tells of phosphorus, arsenic, antimony, and bismuth.]

CRASS. "A History of the Match Industry," *Journal of Chemical Education*, Vol. XVIII, pp. 116, 277, 316, 380, 428.

CUNNINGHAM. "Sulfur," *Journal of Chemical Education*, Vol. XII, pp. 17, 83, 120. [A series of three articles. Very complete and well illustrated.]

DARROW. *The Story of Chemistry.* [Chapter VI tells of agriculture and war.]

FABRE. *The Wonder Book of Chemistry.* [Chapter X, "Burning Phosphorus," and Chapter XXIV, "Sulfur," are very elementary; they are given in the form of a conversation.]

FOSTER. *The Romance of Chemistry.* [Read Chapter XII, "Sulfur, a Pillar of Industry"; Chapter XIII, "Nitrogen, Fertilizers, and Explosives"; Chapter XIV, "Phosphorus and Related Elements."]

HOLMES. *Out of the Test Tube.* [Read Chapter XXX, "The Farm as a Factory."]

HUXLEY and ANDRADE. *More Simple Science.* [Chapter IV, "Soils," and Chapter V, "Agriculture," contain valuable information about soils, fertilizers, and plant life.]

MORRISON. *Man in a Chemical World.* [Chapter IV, "Feeding Millions," gives valuable information about the materials used in the manufacture of fertilizers.]

SLOSSON. *Creative Chemistry.* [Chapter III, "Feeding the Soil," tells an interesting story.]

WAGGAMAN. "The Phosphate Rock Industry in the United States," *Journal of Chemical Education*, Vol. X, pp. 391 and 476. [A series of two articles. Complete and well illustrated.]

WEEKS. *The Discovery of the Elements.* [Read about the discovery of the elements that make up the sulfur family and the nitrogen family; see index for pages.]

The Science Leaflet. [No. 6 of recent volumes tells of the members of the nitrogen family. No. 10 tells of phosphorus and related elements.]

World Book Encyclopedia. [Contains an interesting article about matches, with many pictures.]

Unit Nine. Sand in Industry: Big and Very Little Particles

THIS is a unit of surprises. Part of it centers about the second most abundant element, found not (like oxygen) in the air but in the ground beneath our feet. We discover a close relationship between ordinary sand and glowing jewels. We start with the oldest industries in the world's long history — making bricks and crude pottery — and find these same industries still of greatest importance. But how they have changed! It is hard to believe that chemistry has so helped them to develop that they give us our beautiful dishes, our colorful glasses and enamels, and other articles without number that we use every day. Sand and its compounds are the source of all such things.

And then we enter the borderland between physics and chemistry and come upon a new discovery: The chemical conduct of any kind of matter, as well as its physical properties, is greatly modified by the size and shape of its particles. The chemistry of very small particles is called *colloidal chemistry*. This interests the biologist as well as the chemist, for much of the matter of living organisms is made up of these very small particles.

We shall also be surprised to learn how large a part of modern manufacturing is based on our knowledge of colloidal chemistry.

CHAPTER XXXIV

Silicon and Boron

[Two Elements Whose Compounds Are of Great Importance in Industry]

SILICON

Silicon — One of the Abundant Elements. We have learned that oxygen is by far the most abundant of all the elements. In round numbers we may say that, so far as we can tell, there is as much oxygen in the world as of all the other elements combined. But what element comes second? It is silicon, the element that makes up more than one fourth of the earth's crust (p. 29).

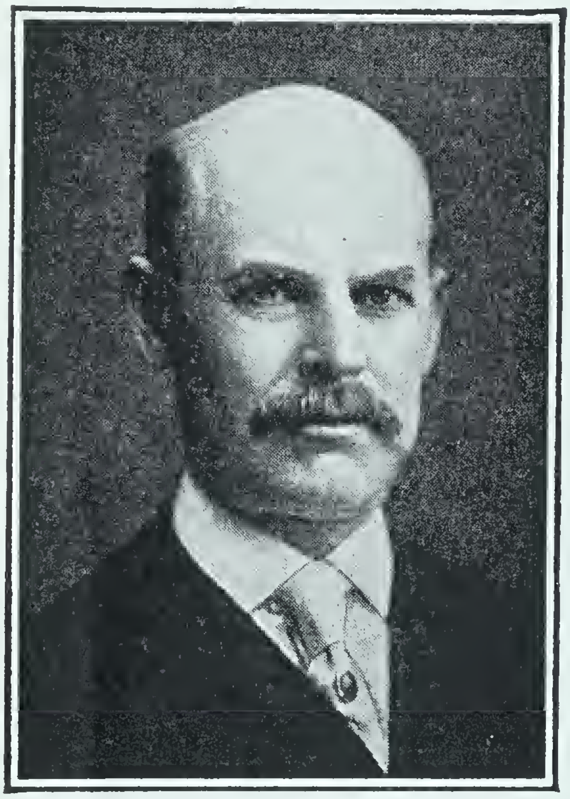


FIG. 276. Edward Goodrich Acheson (1856–1931)

An American scientist who discovered commercial methods for the manufacture of carborundum, graphite, and a number of similar products of great use in the industrial world

Indeed, more than any other element it seems to be the framework of the structure of most mineral matter. It occurs in nature chiefly in the form of silicon dioxide, SiO_2, or as salts of silicic acids; and these compounds make up almost all the common rocks and soils except limestone.

What is silicon like? Although silicon is so abundant, it is seldom seen in its pure form. This is because it never occurs free in nature. It is true that it can be easily prepared, but it has few uses except for making certain varieties of iron and steel, as we shall learn later. The pure, crystallized element is a dark-gray, metallic, brittle solid. Like carbon, it is known as a black powder as well as in the crystalline form.

The preparation of the element. Silicon is prepared from ordinary sand, which is largely silicon dioxide (SiO_2). This

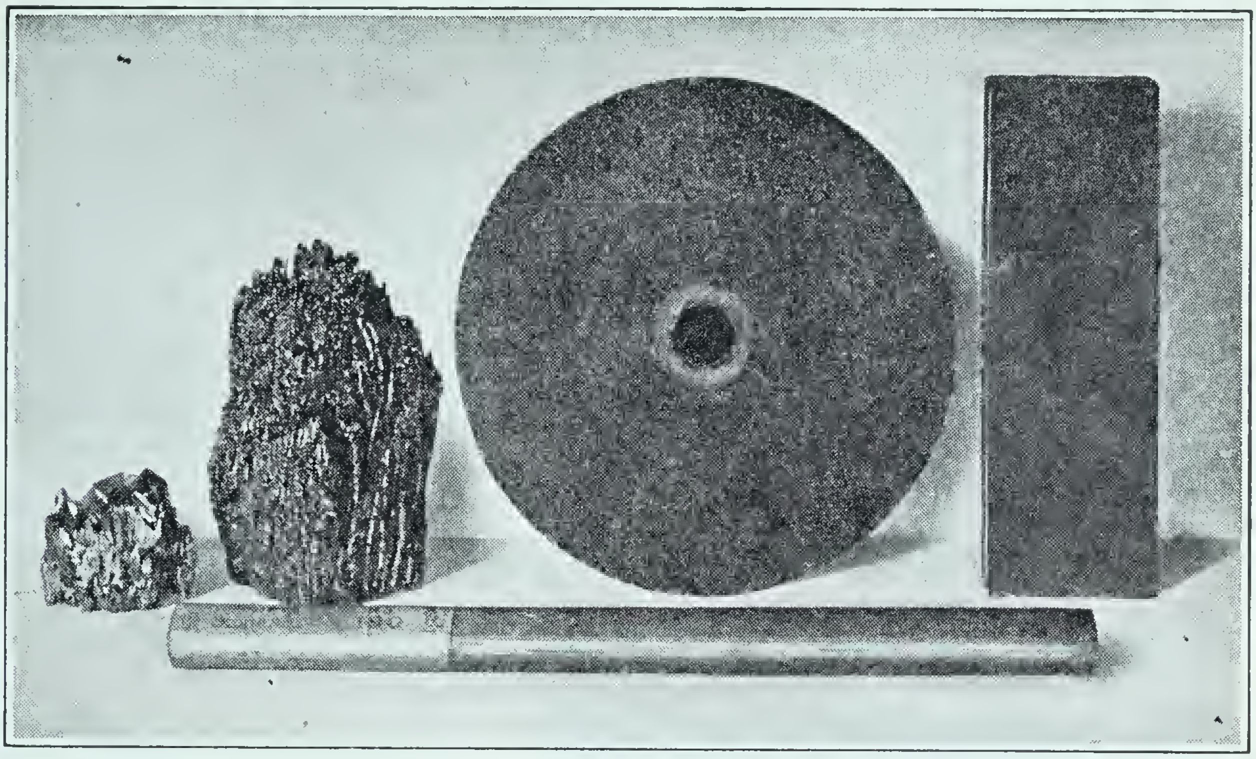


FIG. 277. Crystals of carborundum and different abrasive utensils made of carborundum

oxide is reduced with either aluminum or carbon, and a high temperature is required. With carbon the equation for the reaction is as follows:

$$SiO_2 + 2\,C \longrightarrow Si + 2\,CO\uparrow$$

Its important reactions. Silicon readily unites with chlorine, forming the chloride $SiCl_4$, and with fluorine to form SiF_4, the gaseous compound given off when glass is etched with hydrofluoric acid (p. 336). At high temperatures it combines directly with carbon and many of the metals to form compounds called *silicides*.

Carbon silicide, or silicon carbide (SiC), a very hard compound. This compound, commonly known by the trade name *carborundum*, was first made on a large scale by Edward Acheson (Fig. 276). When sand (SiO_2) is heated with carbon, silicon is set free, but under the proper conditions it at once combines with excess of carbon to form silicon carbide:

$$\begin{aligned} SiO_2 + 2\,C &\longrightarrow Si + 2\,CO\uparrow \\ Si + C &\longrightarrow SiC \end{aligned}$$

This reaction is carried out in large electric furnaces similar to the ones used in making graphite (Fig. 96), and great quantities of the carbide are made at Niagara Falls, where electric power is cheap.

Silicon carbide is a very hard substance, being exceeded in this property only by the diamond and one or two rare compounds; and it is this hardness that makes it so valuable. It is used as an *abrasive*, that is, as a material for grinding and polishing other hard substances (Fig. 277).

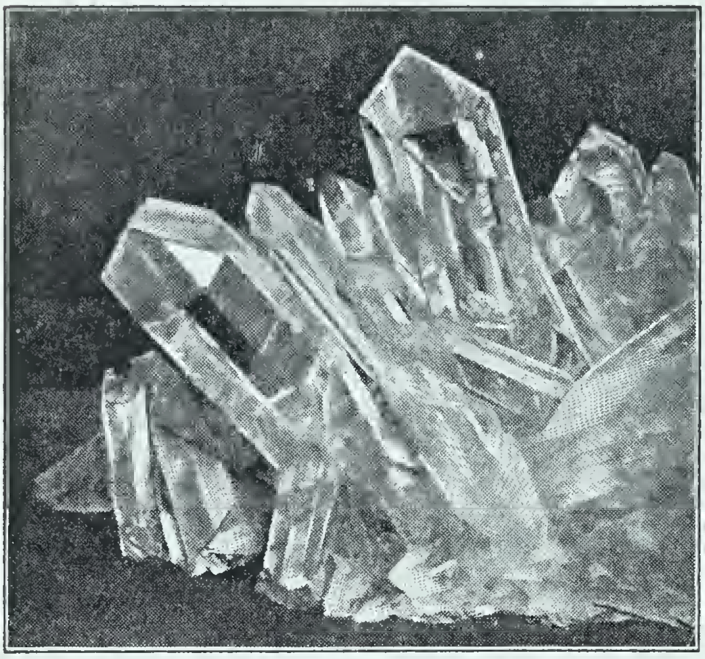


FIG. 278. A cluster of quartz crystals

Silicon dioxide (SiO_2). This compound, known also as *silica*, is found in a great variety of forms in nature, in both the amorphous and the crystalline state. We know it best as ordinary sand, some deposits of which are nearly pure silicon dioxide. As *quartz* it is found in beautiful six-sided prisms (Fig. 278), sometimes of great size. When pure it is perfectly transparent and colorless. Some colored varieties are given special names, as *amethyst* (violet), *rose quartz* (pale pink), *smoky quartz* (brown), *milky quartz* (opaque). Other varieties of silicon dioxide, some of which also contain water, are *chalcedony*, *onyx*, *jasper*, *opal*, *agate* (Fig. 279), and *flint*. *Sandstone* is largely silicon dioxide.

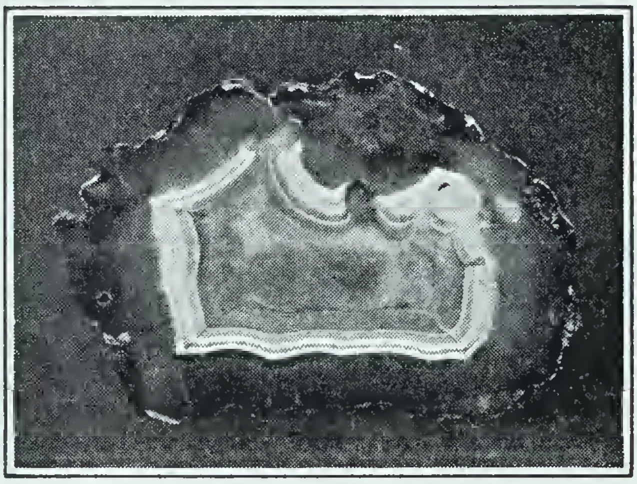


FIG. 279. A typical sample of agate (polished)

The properties of silicon dioxide. When it is made by chemical processes silicon dioxide, or silica, is an amorphous white powder. In the crystallized state it is very hard and has a density of 2.65. Pure silica begins to soften at about 1600°, and somewhat above this temperature it can be drawn out into threads and blown like glass into tubes and small vessels (Fig. 280). Larger vessels are molded, or "built up." These articles are attacked by

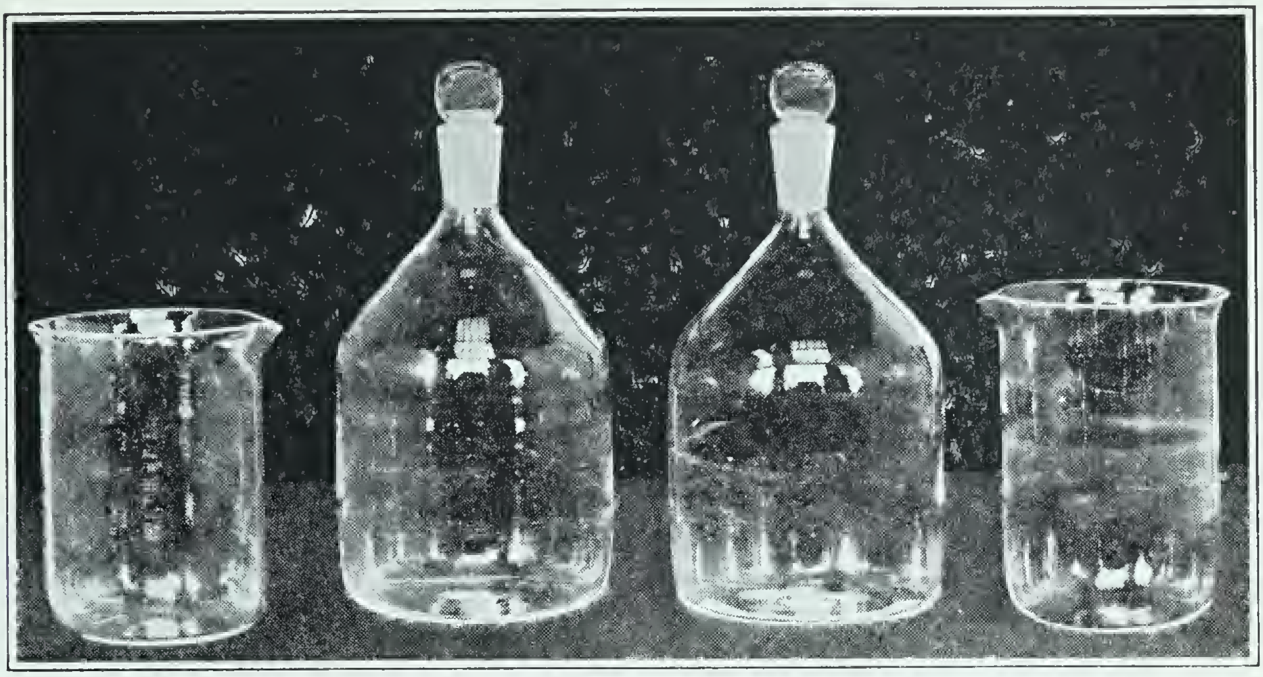


FIG. 280. Beakers and bottles made of quartz

comparatively few ordinary reagents, and expand or contract very little with even very great changes in temperature. On this account quartz vessels can be heated red-hot and plunged into cold water without cracking. Unfortunately they are expensive.

How silicon dioxide acts. Silicon dioxide is very inactive. It is insoluble in water and most acids, but is readily acted upon by hydrofluoric acid (p. 336). When it is heated to high temperatures with compounds of the metals, especially the carbonates and sulfates, *silicates* (salts of silicic acids) are formed as follows:

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2\uparrow$$
$$Na_2SO_4 + SiO_2 \longrightarrow Na_2SiO_3 + SO_3\uparrow$$

These are important reactions in making glass (p. 399).

Acids of silicon. There are two simple acids of silicon: *orthosilicic acid* (H_4SiO_4) and *metasilicic acid* (H_2SiO_3). Orthosilicic acid is formed as a jellylike substance when its salts, the orthosilicates, are treated with strong acids. If one attempts to dry this jelly, it loses water, passing into metasilicic acid (common silicic acid):

$$H_4SiO_4 \longrightarrow H_2SiO_3 + H_2O$$

When dried still further, metasilicic acid breaks up into silica and water:

$$H_2SiO_3 \longrightarrow H_2O + SiO_2$$

There are a great many complex acids of silicon that are of no importance in themselves. The only reason for mentioning them is because their salts are of so much importance. They are formed from two or more molecules of orthosilicic acid, which combine, with loss of water, thus:

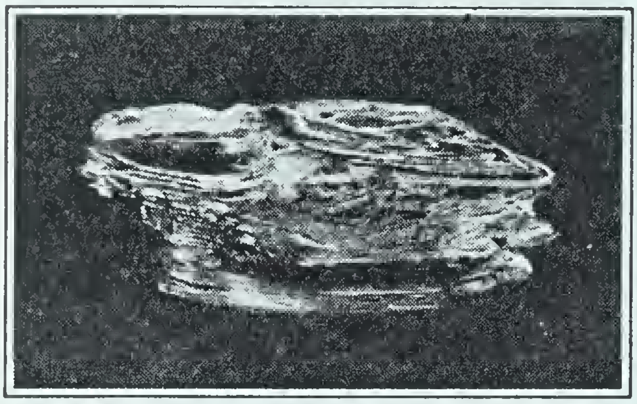


Fig. 281. A typical sample of mica

$$3\ H_4SiO_4 \longrightarrow H_4Si_3O_8 + 4\ H_2O$$

Salts of silicic acids — the silicates. The earth must have been once a hot liquid mass that gradually cooled, forming a solid crust of igneous rocks. Various salts of the silicic acids made up the great bulk of these rocks, the most important of which are as follows:

1. ***The feldspars.*** There are several kinds of feldspars, the most common of which is orthoclase ($KAlSi_3O_8$). They are used in the manufacture of porcelain and similar products.

2. ***Mica.*** The name *mica* is given to a number of silicates all of which can be split into thin sheets (Fig. 281). These sheets are used as insulators in various electrical machines. Powdered mica has various uses, such as the manufacture of wall-paper coating and certain kinds of roofing. It is the common "Christmas-tree snow."

3. ***Granite.*** This well-known building stone varies in composition, but consists mainly of crystals of feldspar and mica cemented together by silica (Fig. 282).

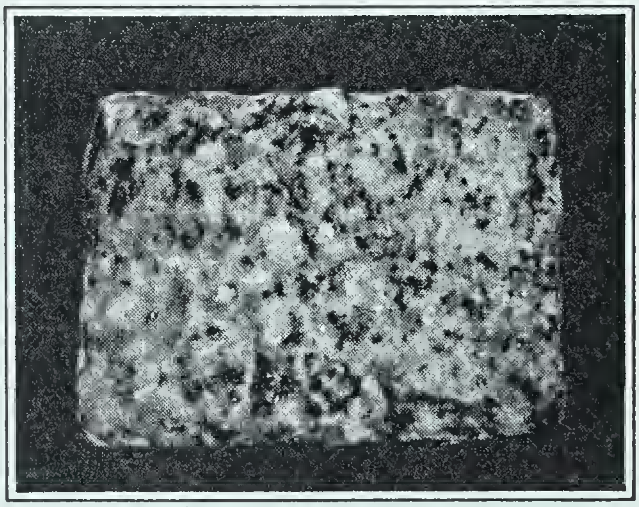
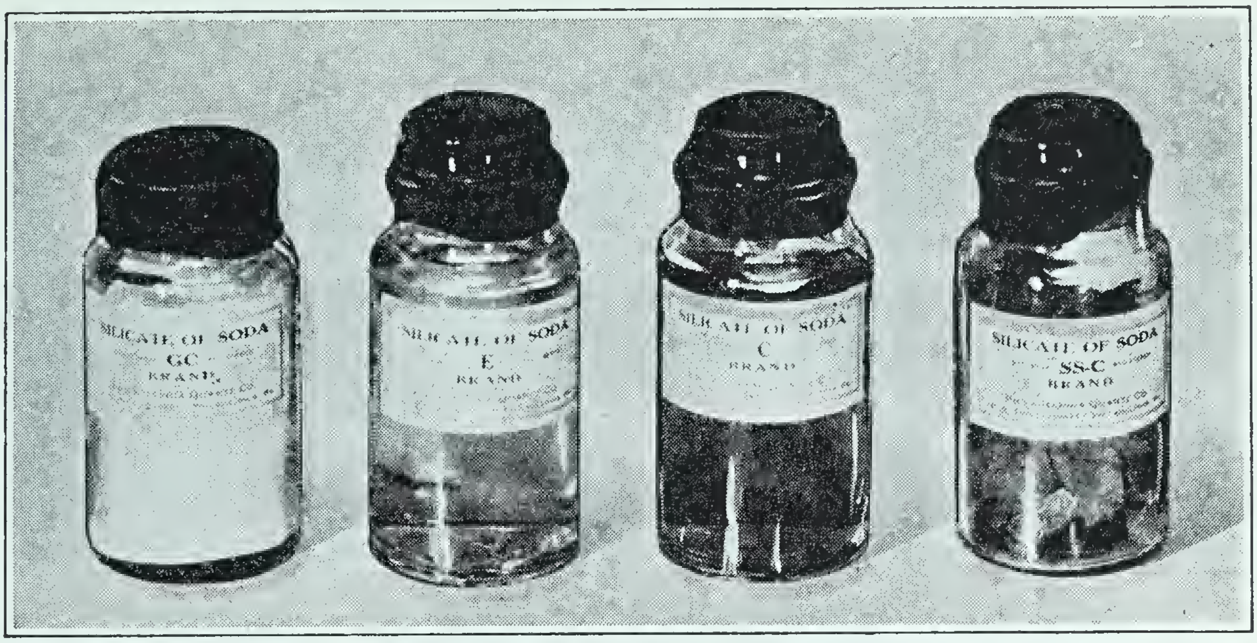


Fig. 282. A sample of granite

Water glass. Sodium silicate (Fig. 283) and potassium silicate differ from the silicates of the other metals in that they are soluble in water. *Water glass,* a thick, sticky liquid, is



Industrial and Engineering Chemistry

FIG. 283. Some different samples of silicate of soda sold on the market

a solution of a mixture of sodium silicates made by melting sand with sodium carbonate. It has many uses. For example, it is used to give a glazed, waterproof surface to porous materials, such as wood, stone, and plaster; to make curtains noninflammable; as a glue for mending glass and pottery and for gluing strawboard boxes; and in making cheap soaps.

BORON

An element of few uses. Boron is a dark-gray solid, difficult to prepare, and in the free state but little used. It is found in nature in many minerals and in many places, but at present the world's supply of boron compounds comes from the Mojave Desert in California. The two sources of production are the mineral *kernite,* also called *rasorite* ($Na_2B_4O_7 \cdot 4\,H_2O$), and the salts of Searles Lake (Fig. 284). The most important compounds of boron are boric acid, boric oxide, and borax.

Boric acid (H_3BO_3). This is a white solid, slippery to the touch, and having exceedingly feeble acid properties. It is a mild antiseptic and is used in medicine, especially as an eyewash.

Boric oxide (B_2O_3). When boric acid is heated, it loses water and forms the anhydride, B_2O_3:

$$2\,H_3BO_3 \longrightarrow B_2O_3 + 3\,H_2O$$

FIG. 284. Searles Lake, California

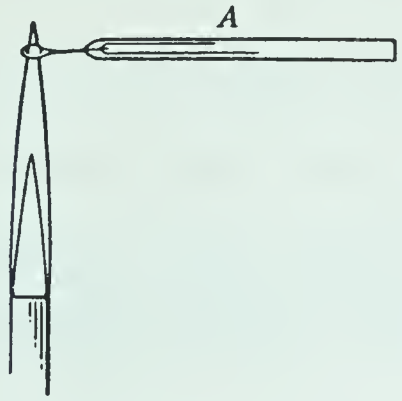
Searles Lake is really a salt bed in the desert and most of the time contains no water. Both borax and potassium compounds are obtained from these salt beds

This is a clear, glassy solid that resembles silica both in its appearance and in its chemical conduct.

Sodium tetraborate ($Na_2B_4O_7$). If we add sodium hydroxide to boric acid, we do not get the sodium salt we should expect — namely, Na_3BO_3 — but one that has the formula $Na_2B_4O_7$ and is called *sodium tetraborate.* When this is crystallized from water at ordinary temperatures, a hydrate is deposited having the formula $Na_2B_4O_7 \cdot 10\,H_2O$. This white, well-crystallized hydrate is called *borax.*

Borax. Borax is the most important compound of boron. It is prepared chiefly from kernite by dissolving the mineral in water and allowing it to crystallize at ordinary temperatures.

When borax is heated, it swells up in a sort of froth, owing to the escape of steam, and then soon melts to a clear glass, which has the property of easily dissolving many metallic oxides; and this fact is turned to account in working with metals. When two pieces of metal are to be joined by the use of some kind of solder, the surfaces must be clean and free from oxide. Brass is joined by melting borax over the joint, to clean the metal, and then using a low-melting brass as a solder (brazing). Metallic oxides dissolved in melted borax often color the borax glass with characteristic tints. On this account little beads of borax are used in testing for the presence of such metals (Fig. 285).



One end of a platinum wire is sealed in the glass handle *A*, the other end being made into a loop. The loop is then heated and dipped into powdered borax, and the borax heated in the tip of a Bunsen flame until it melts, forming a clear bead. A small particle of the substance to be tested is then brought in contact with the bead, and the bead and the adhering particle again heated until the two form a uniform glass. When the bead is cool, its color is noted

FIG. 285. Borax-bead test

Borax is extensively used as a constituent of glass, and of enamels and glazes for both metalware and pottery. It is often used in our homes to soften hard water, and as a mild alkali instead of soap.

CHAPTER SUMMARY IN QUESTION FORM

1. To what element is silicon second in abundance?

2. Sand and sandstone are composed largely of what compound?

3. What general name is given to compounds containing silicon and some other element?

4. (*a*) By what other names is silicon carbide known? (*b*) Give its chief property and uses.

5. Name three varieties of silicon dioxide found in nature.

6. A beaker made of quartz is similar in many respects to one made of glass, but differs in one important property. What is this property?

7. Though insoluble in most reagents, silica dissolves in a certain acid. (*a*) Name the acid and (*b*) state what practical use is made of this reaction.

8. (*a*) What two compounds are formed when a mixture of silicon dioxide and sodium carbonate is heated to a high temperature? (*b*) What practical use is made of this general reaction?

9. Give the names and formulas of two simple acids of silicon.

10. Show by an equation how complex silicon acids are formed from the simple acids.

11. (*a*) What name is given to a solution of sodium silicates? (*b*) Name two uses of this solution.

12. What locality is the source of the greater part of the world's supply of boron?

13. Give the name and composition of the mineral which is the chief source of all boron compounds.

14. (*a*) Give the name and formula of the most important compound of boron, and (*b*) state four uses of this compound.

THOUGHT QUESTIONS

1. Give an example in which an electric current causes a chemical reaction (*a*) by the heat the current produces; (*b*) by electrolysis.

2. How could you distinguish between a quartz crystal and a diamond?

3. Could you tell by the physical properties of a compound whether it contains water of hydration?

4. Calculate the molecular weight of each of the compounds represented by the following formulas: (*a*) $BaCl_2 \cdot 2\,H_2O$; (*b*) $Na_2B_4O_7 \cdot 10\,H_2O$. (*c*) Name each of the compounds.

5. Many salts, such as sodium tetraborate ($Na_2B_4O_7$), when crystallized from water are found to have formed compounds with the water. (*a*) What is the general name for such compounds (p. 116)? (*b*) What is the name given to the water held in combination? When such compounds are heated, the water is expelled. (*c*) What name is given to the resulting compound?

6. Illustrate the facts stated in question 5 by reference to borax.

OPTIONAL EXERCISES

1. Carbon and silicon are in the same group in the periodic arrangement of the elements (p. 323). Study the formulas and reactions of their compounds and see if you can find any points of resemblance.

2. When you buy one ton of borax, what weight of water are you buying?

CHAPTER XXXV

The Silicate Industries

[Very Important Industries That We Should Know More About]

What are some of the important uses of the silicates? In our study of silicon we learned that, while the element itself has few uses, the salts of the silicic acids, the silicates, are of very great importance.

For example, count over the materials of which our homes are made. The bricks in the walls and chimneys, the glass in the windows, the tiles on the roof and hearth, the plaster on the walls, the cement in the foundations and walks — all are composed chiefly of silicates. So, too, many of the household utensils and ornaments, such as crocks and jars, glassware, and dishes of all kinds, are made from silicates.

The industries that manufacture all these things are called the *silicate industries*, or, more often, the *ceramic industries.* Fig. 286 shows a few of the products that are made by these industries.

Glass — what it is. Glass is a mixture of certain silicates that has been completely melted and then cooled. It is really an undercooled liquid (p. 54), although it is as rigid as a true solid. The silicate mixture is made by melting together at a very high temperature compounds that contain the necessary metals (such as sodium and calcium) together with an excess of sand (SiO_2). The following equations illustrate the reactions that take place:

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2\uparrow$$
$$Na_2SO_4 + SiO_2 \longrightarrow Na_2SiO_3 + SO_3\uparrow$$
$$CaO + SiO_2 \longrightarrow CaSiO_3$$

The excess of sand then combines with these simple silicates to make the mixture of more complex ones that we call glass.

The different kinds of glass. By choosing the right materials many varieties of glass can be made. Window glass and bottle glass are chiefly mixtures of silicates of sodium and calcium made by heating sodium carbonate (Na_2CO_3),

Fig. 286. Samples of some of the many products made from silicates

lime (CaO), and sand. Sometimes sodium sulfate is used in place of sodium carbonate, and limestone in place of lime.

For a glass more resistant to active chemicals the sodium carbonate is wholly or partly replaced by potassium carbonate, and some boric acid is added along with the sand. So the resulting glass is a *borosilicate* of the metals present. A sodium-aluminum-borosilicate, containing a large percentage of free silica, is known by the trade name *Pyrex glass.* Such a glass is able to stand sudden changes of temperature and is not easily broken. Optical glass owes its brilliancy to the presence of lead silicate. Cheap imitations of gems are made from glass rich in lead silicate (paste).

The "safety glass" used so largely in automobiles is made by putting a sheet of celluloid or some similar material between two plates of glass and heating the combination under pressure. It might be called a celluloid-glass sandwich.

The manufacture of glass — how it is worked into the desired shape. The raw materials used in making glass are heated in large furnaces until the reactions are complete and the liquid glass is formed. As this cools it becomes very thick, or *plastic*, and while in this condition can be worked into a great variety of shapes that keep their form when cold. The way in which the melted mixture is handled in the glass factory depends upon the object to be made.

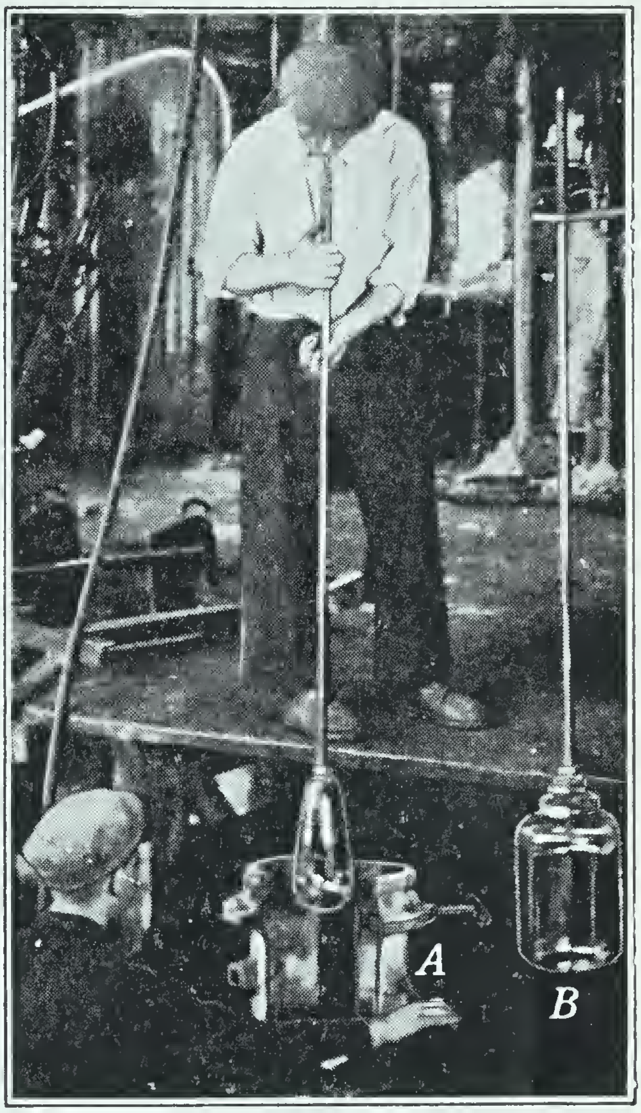


Fig. 287. Steps in the making of a beaker

Many articles such as bottles and beakers are made by blowing the plastic glass into hollow molds of the desired shape. Fig. 287 shows how a beaker is made by this process. The mold is first opened, a lump of plastic glass on the end of a long, hollow tube is lowered into it (*A*), and the mold is then closed. By blowing into the tube, the glass is forced into the shape of the mold, just as the inner tube of an automobile tire is blown out against the sides of the casing. The mold is then opened, and the partly formed beaker lifted out (*B*). The top of this is then cut off at the proper place and the sharp edges are rounded in a flame. Fig. 288 shows a glass bottle in its mold. Complex articles not readily molded are blown into the desired shape by skilled glass-blowers (Fig. 291).

Such articles as bottles and electric-light bulbs are now made by machinery in which the plastic glass is blown in the mold by compressed air. These machines are very efficient, a single one making as many as twenty thousand electric-light bulbs per hour.

Glass fibers. By dipping the end of a rod into melted glass and then drawing it out very fast, glass sticks to the rod and is drawn out to a thread of any desired thickness. Fibers only one tenth the diameter of a human hair have been made in this way. *Glass wool* is a mass of fibers of glass and is used for heat insulation in the walls of buildings and refrigerators. Glass cloth, woven from such fibers, is used for fireproof curtains, for electrical insulation, and as filters for corrosive liquids.

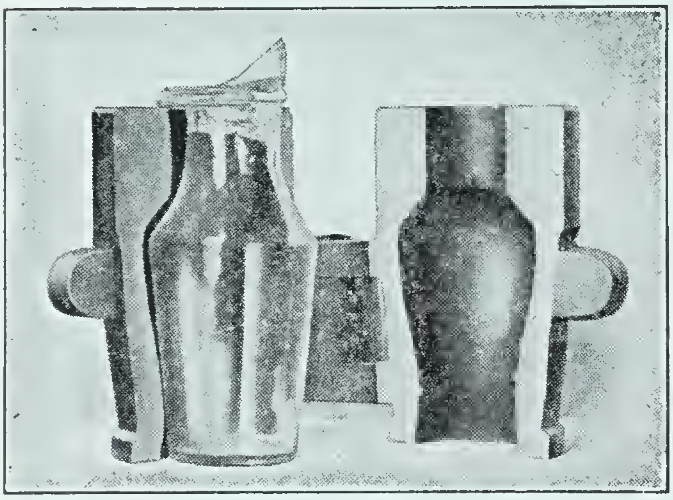


Fig. 288. A glass bottle in its mold

The mold has been opened and the bottle is ready to be removed and finished by rounding its mouth

Annealing of glass. If liquid glass cools rapidly, it becomes very brittle. In order to counteract this, glass articles, always hot when first formed, are placed in an oven and slowly cooled. This process is known as *annealing*.

How window glass is made. Window glass was long made by blowing plastic glass into the form of cylinders. These were then cut lengthwise, heated until soft, and flattened out into sheets of glass — much as a cylinder of paper cut lengthwise opens out into a sheet.

At the present time the glass is worked directly into continuous sheets, which are then cut into the desired size and shape. One of the chief methods of doing this is shown in Figs. 289 and 290. In the manufacture of plate glass the plastic material is poured onto a metal surface, rolled into flat slabs, and slowly cooled (annealed). The surfaces of the sheets are then ground smooth and finally polished.

How glass is colored. A small percentage of certain elements (usually metals) gives characteristic colors to glass. For example, cobalt compounds give a blue color; those of manganese, pale purple (amethyst tint). The beautiful ruby-red color of much of the glass we admire in cathedral windows is due to a small percentage of gold. Cuprous oxide and selenium also make glass red. The red color of taillights of most automobiles is due to selenium. The cheaper grades of sand contain iron, and objects made from this are colored green from the ferrous silicate formed. The addition of a suitable oxidizing agent, such as manganese dioxide, changes the ferrous silicate to the ferric compound, which gives a less objectionable yellowish tint to the glass.

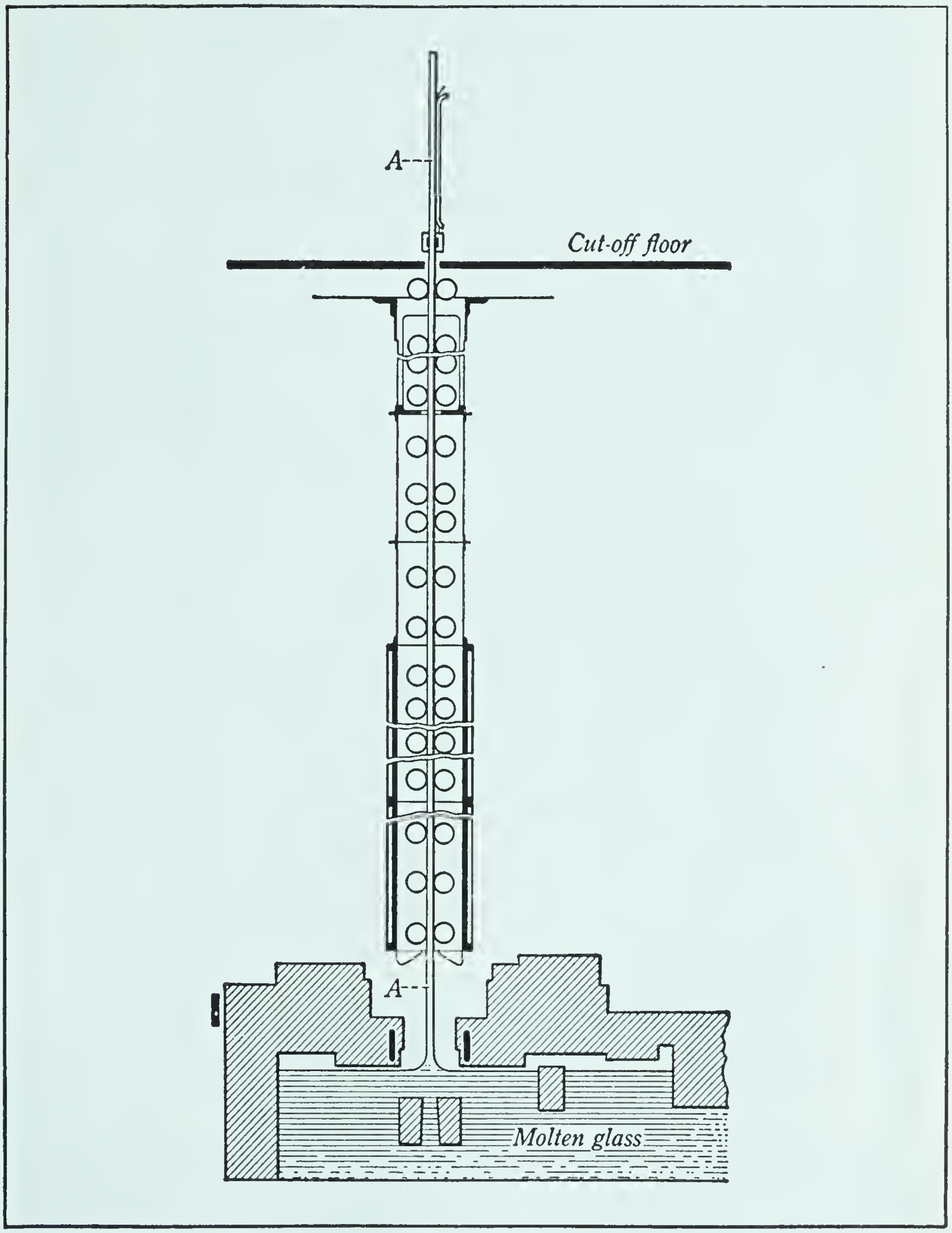


Fig. 289. Sheets of window glass (*A*, *A*) in the making

A rod of proper length is dipped into the molten glass and slowly raised. The thick molten glass clings to the rod, and a continuous sheet of the glass is drawn upward between the rollers, which are adjusted so as to make it of the right thickness. The glass becomes cooler and more rigid as it rises, so that when it passes the "cut-off floor" it can be cut into sheets (see Fig. 290)

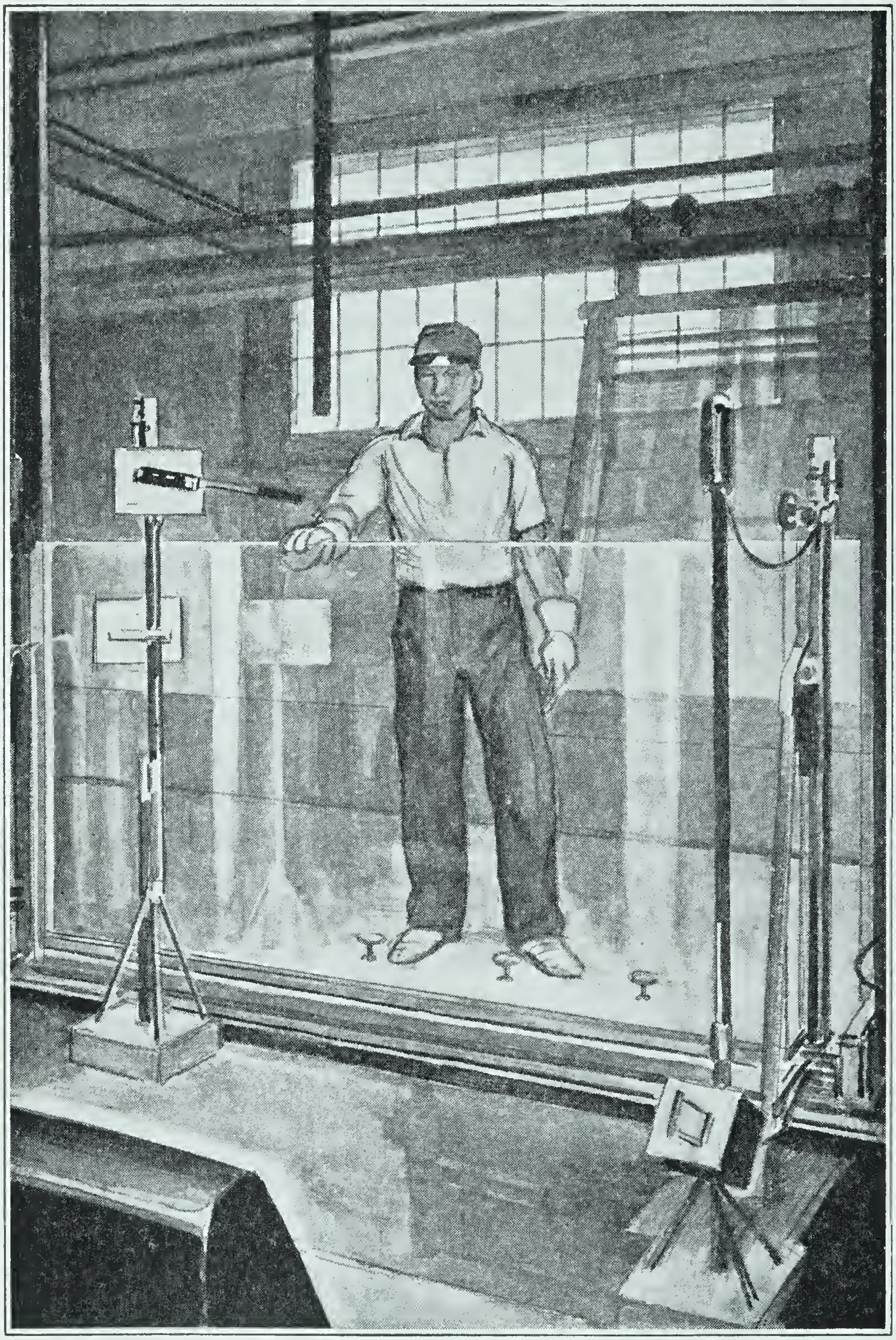


Fig. 290. The manufacture of window glass

The figure shows the sheet of glass as it emerges from the "cut-off floor," shown in Fig. 289. The operator cuts it into large plates by automatic machinery. Each plate is then cut into any desired sizes. (Courtesy of the Pittsburgh Plate Glass Co.)

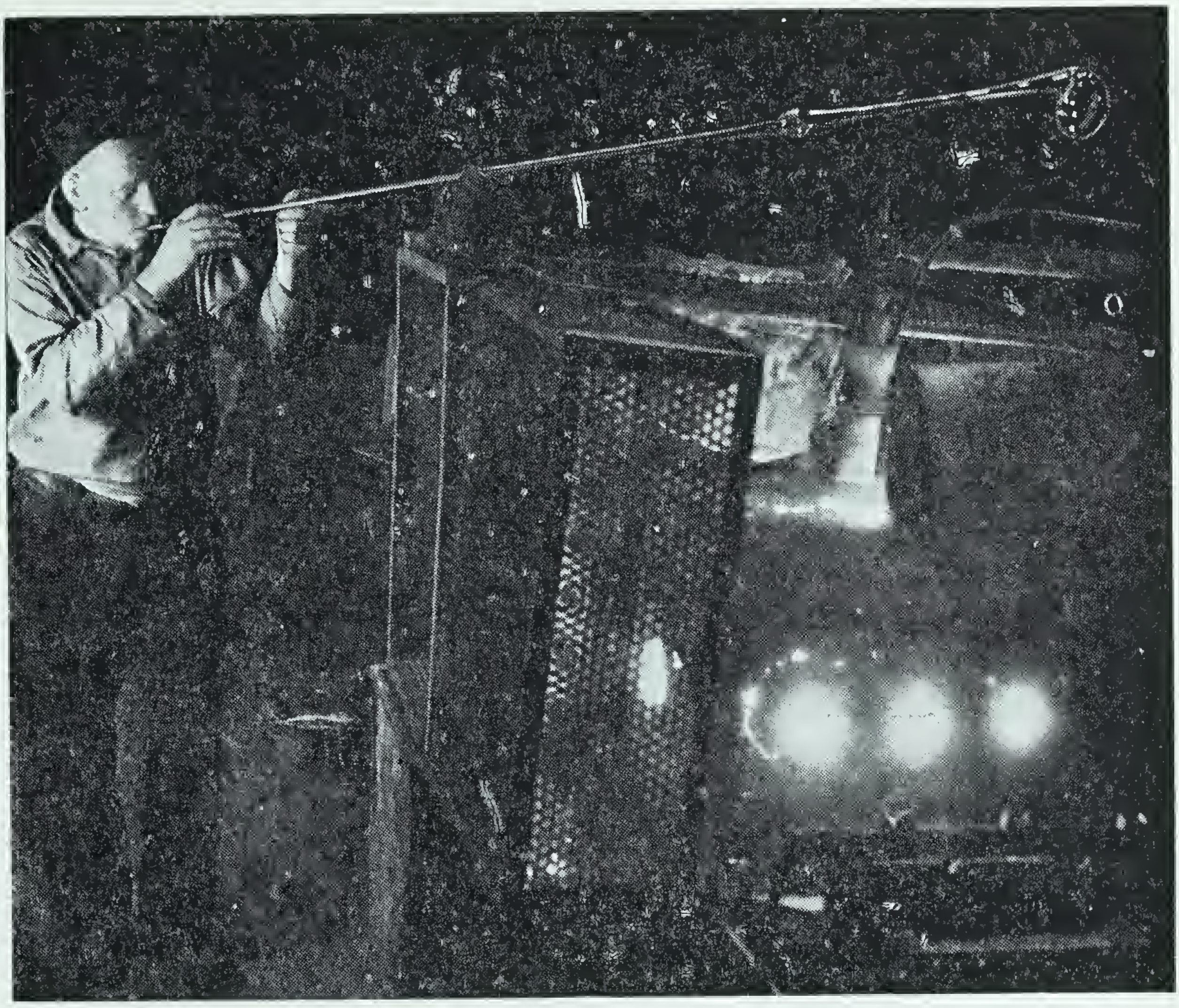


FIG. 291. Making a retort by blowing the plastic glass into the desired shape

Glass and ultraviolet light. Ordinary window glass does not let through all the sunlight that falls upon it, but cuts off completely the ultraviolet rays, that is, the radiation of shorter waves than those of the visible spectrum (Fig. 194). This is the part of the sunshine that seems to have the most health-giving value. Great efforts are being made to develop a window glass that will transmit the ultraviolet light as well as the visible light, and much progress is being made.

PRODUCTS MADE FROM CLAY

What is clay? In our study of silicates (p. 394) we learned that the igneous rocks from which the soils were formed were largely feldspars. One of the most common of these has the formula $KAlSi_3O_8$. When these are slowly decomposed by weather agencies, soluble compounds of potassium are formed and dissolve into the soils. At the same time an insoluble aluminum silicate is left behind, which is carried by running water and is sometimes deposited in beds of streams in nearly pure condition. This is known as *kaolin* and has the formula $Al_2Si_2O_7 \cdot 2\,H_2O$. More often the aluminum silicate becomes mixed with sand and other materials and is then called *clay*.

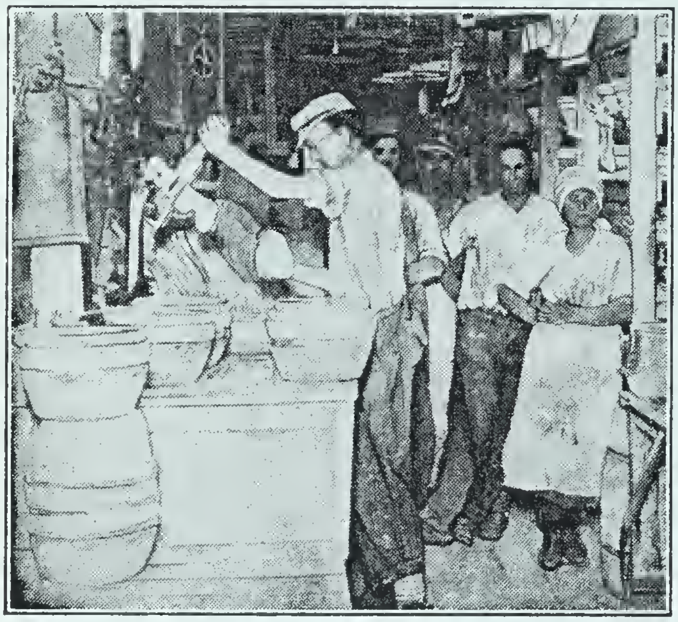


FIG. 292. Molding pottery

Pressing plastic clay into molds by a hand press

Brick and common tile. The crudest kinds of clay products, such as porous brick and drain tile, have little chemistry involved in their manufacture. A suitable clay is molded into the required form, dried, and then burned in a kiln, but not to a temperature at which the materials soften. In this process the nearly colorless iron compounds in the clay are oxidized into colored compounds that give the usual red color to these articles. In making *vitrified brick* the temperature is raised to the point at which melting just begins.

White pottery. This name is given to a variety of articles, from the crudest porcelain to the finest chinaware. Although the manufacture of these articles differs in details, the main processes are the same and may be described under three heads: (1) the body of the ware, (2) the glaze, and (3) the decoration.

1. ***The body of the ware.*** The materials used consist of an artificial clay made by mixing kaolin, clay, and powdered feldspar. This mixture is plastic and is worked into the desired shape by molds (Fig. 292) or on a potter's wheel. The ware is then dried and burned in a kiln (Fig. 293), and in this form is known as *bisque*. This is usually porous, and must therefore be glazed so that it will not soak up water.

2. ***The glaze.*** The glaze is a fusible glass made of quartz, feldspar, and various metallic oxides, often mixed with a little boric oxide. These materials are finely ground, and are

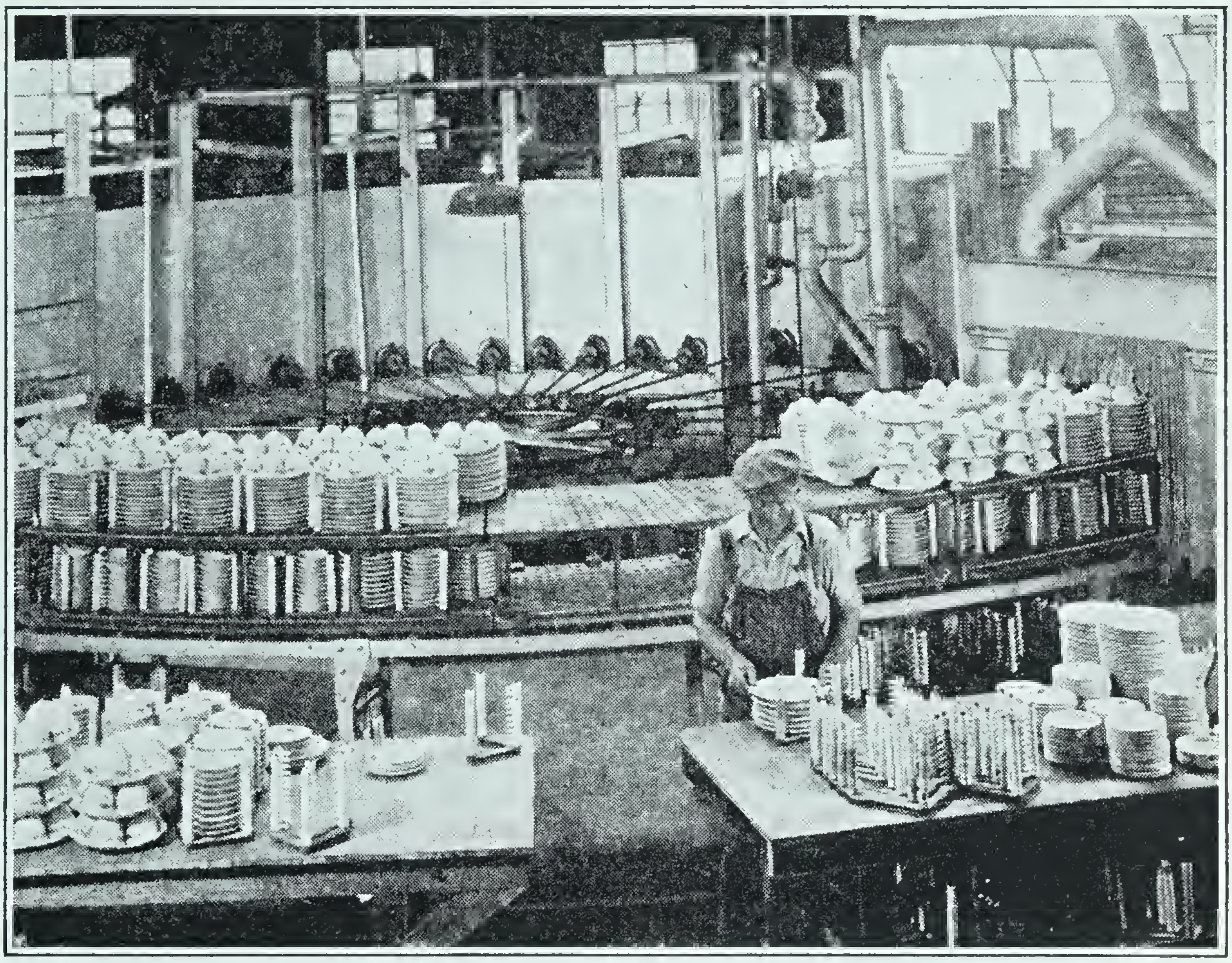


Fig. 293. The manufacture of silicate wares, such as plates

The picture shows the burning of the wares in a kiln. Various kinds of kilns are used, but the one shown is circular in shape. The wares are placed on the shelves that slowly revolve through a highly heated kiln. As the wares return to the open space they are replaced by unburned wares, and the process continues

mixed with water to form a paste (slip). Sometimes the materials are first melted together to a glass (frit), which is then powdered and made into the paste. The bisque is dipped into the glaze paste, dried, and fired until the glaze materials melt and flow evenly over the surface.

3. *The decoration.* If the article is to be decorated, the design may be painted upon the body before glazing, or it may be painted upon the glaze and the article fired again, the color pigments melting into the glaze. In the former case the pigments used are, as a rule, metallic oxides of various colors; in the latter case they are often colored glasses.

Enamels. Enamels are glazes melted onto surfaces of various kinds, chiefly metal surfaces, to make the object look like porcelain, and to protect the surface from rust or chemical action. Graniteware cooking vessels, bathtubs, and automobile number plates and makers' designs are examples.

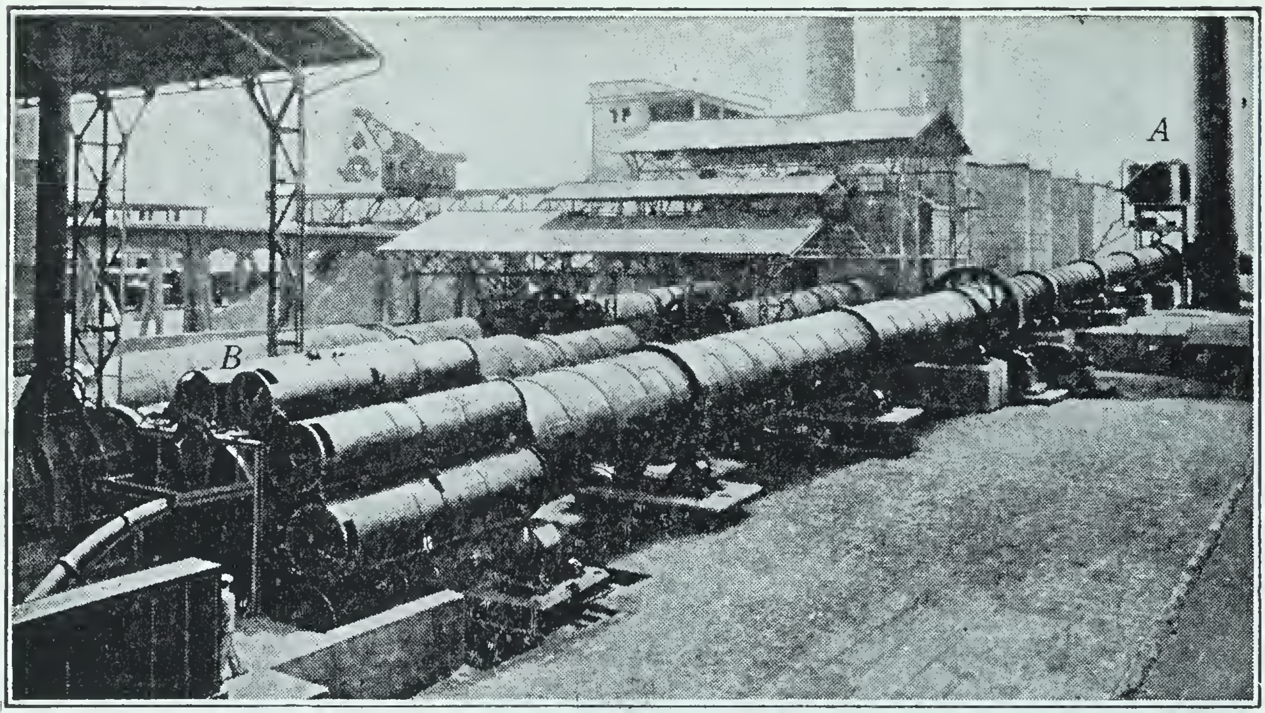


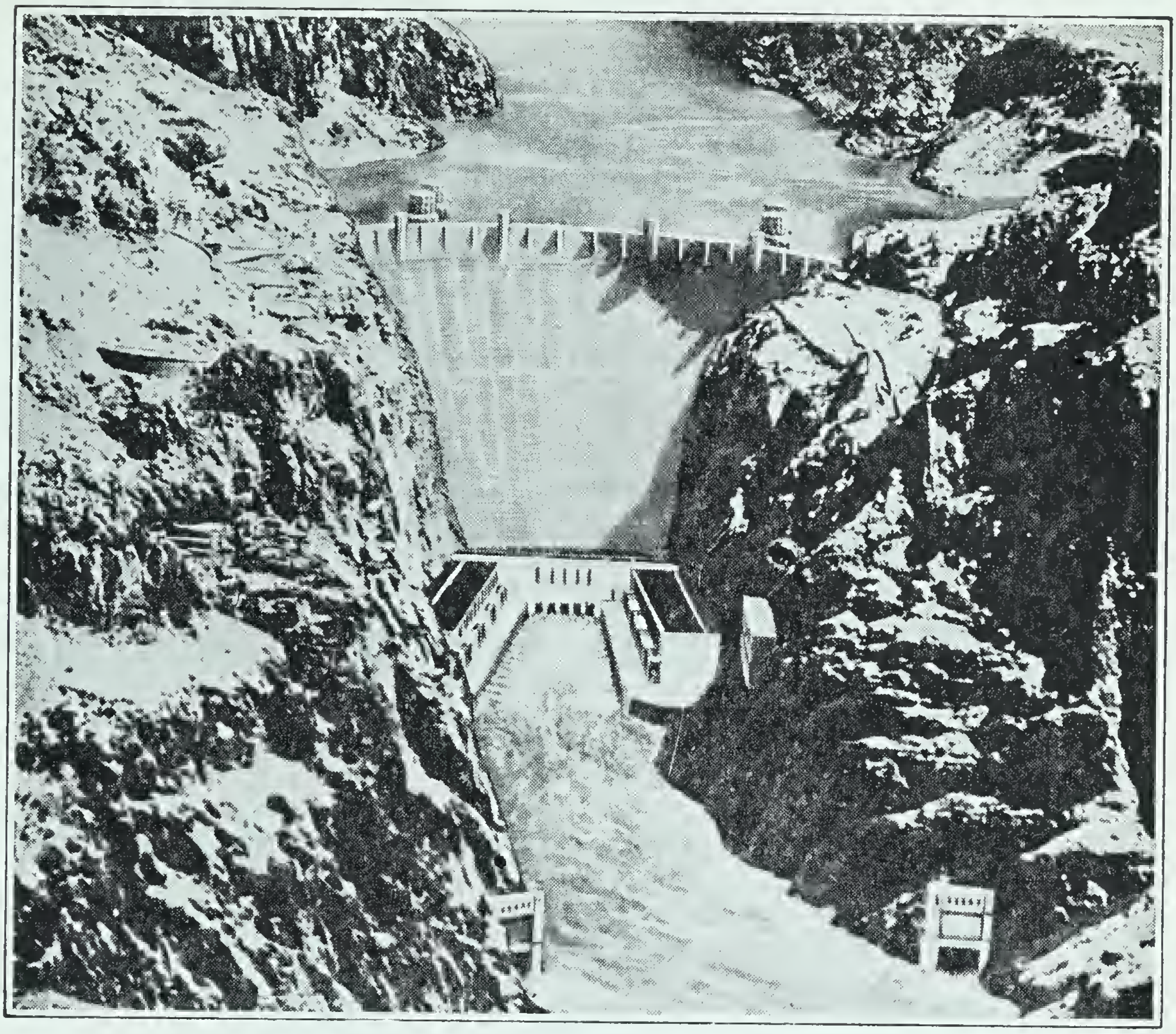
Fig. 294. View of a rotary kiln used in making cement

The tube (kiln), 300 feet long or more, constantly rotates. It slopes down from the far end, *A*, where the raw materials are fed in, to the near end, *B*, so that the materials slowly move forward from *A* to *B*, where the burnt clinker is removed. The fuel (gas or sprayed oil) burns with a hot flame as it enters the kiln at *B*; so the cement materials are increasingly heated until they nearly reach the exit, *B*

Cement. The name *cement* is ordinarily given to those mortars that can *harden in water as well as in air.* These cements are silicate bodies, but have in them much more of metallic oxides and less silica than does glass. When ground fine and mixed with water, they undergo complex reactions which result in making a hard, rocklike mass. A number of different kinds of cements are manufactured, the most important of which is called *Portland* cement.

How Portland cement is made. The materials most commonly used in making cement are limestone and clay or shale, although any product that is similar in composition to these materials may be used.

The materials are coarsely ground separately and are then mixed together in the proper proportions and finely powdered. The mixture is put in a large rotary furnace (Fig. 294) and burned to a temperature just short of fusion. At this temperature it vitrifies, forming balls no larger than a walnut, called *clinker.* Finally the clinker is ground to a fine powder, and the cement is then ready for the market. The mineral gypsum is often added in the process. It acts as a negative catalyst, slowing up the setting of the cement.



Associated Press

FIG. 295. A view of Boulder Dam

This dam, built of reinforced concrete, is located on the Colorado River where the river forms the boundary between Arizona and Nevada. It is 1282 feet in length at its top, and 727 feet high — by far the highest dam ever constructed. It is 660 feet wide at its base and made to withstand a water pressure of 45,000 pounds per square foot

Cement has many uses. The importance of cement in the construction industries increases each year. Mixed with crushed stone and sand, it is the *concrete* used in foundations of buildings, street-paving, road-building, construction of dams, etc. In the building of Boulder Dam (Fig. 295), on the Colorado River, the amount of concrete used "would build a standard paved highway 16 feet wide, extending from Miami, Florida, to Seattle, Washington." Where great strength is needed, iron rods or wire are embedded in the concrete before it sets, and this is called *reinforced* concrete. Remembering the number of dams that have been built or are being projected, the thousands of miles of our smooth-surfaced highways, and the use of concrete in all building operations, we realize the importance of cement.

CHAPTER SUMMARY IN QUESTION FORM

1. Name some of the important industries included under the general heading of "the silicate industries."

2. In a general way, give the composition of glass and the equations for the reactions that take place in its manufacture.

3. Mention (*a*) the different kinds of glass, and (*b*) the general composition of each.

4. What variety of glass is composed of a mixture of (*a*) silicates of sodium and calcium? (*b*) silicates and borates of sodium and aluminum, with much free silica? (*c*) lead and other silicates?

5. Give the steps in making an ordinary beaker by mouth blowing.

6. What is the composition of the safety glass used in automobiles?

7. (*a*) What was the older method of making window glass? (*b*) What is the present method?

8. What element or compound gives the color to (*a*) cheap bottle glass? (*b*) blue glass? (*c*) purple glass? (*d*) ruby-red glass? (*e*) glass used in the taillights of automobiles?

9. What name is given to earth composed essentially of aluminum silicate and sand?

10. What is the difference between kaolin and clay?

11. (*a*) What physical properties have kaolin and clay that make them so useful? (*b*) The manufacture of what articles is based on these properties?

12. (*a*) Why is glass made from ordinary sand green? (*b*) Why are ordinary bricks red?

13. Give the steps in the manufacture of white pottery.

14. Discuss Portland cement under the following heads: (*a*) characteristic property; (*b*) materials from which it is made; (*c*) method of manufacture; (*d*) uses.

THOUGHT QUESTIONS

1. Why not make glass from sand alone?

2. Why not make glass by heating sand with sodium carbonate?

3. Are bricks ever glazed?

4. Would you glaze (*a*) sewer pipe? (*b*) drainage tile?

5. The following words apply to the composition and manufacture of glass. Include them in a paragraph that deals with the subject.

mixture of
undercooled
rigid as
by heating
annealed

OPTIONAL EXERCISES

1. Collect and exhibit to the class samples of the following substances used in the silicate industry: ordinary sand; pure sand; limestone; feldspar. Label the samples so as to show the composition of each.

2. Make a permanent collection of the finished clay products for your school.

CHAPTER XXXVI

The Colloidal State

[The Chemistry of Very Small Particles]

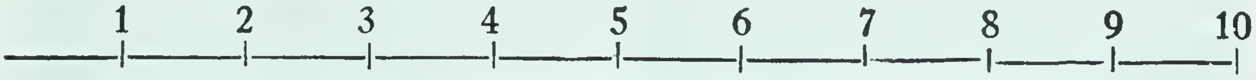
The properties of materials are often modified by their size or shape. We all know that any given kind of matter can be got in pieces of a great variety of sizes and shapes. Rock materials may be as big as mountains or as small as the dust that we do not notice until we see that the furniture needs dusting. We usually buy coal in lumps of various sizes, but many industries use it as a powder.

Now chemists have been surprised to find that the *chemical conduct* of materials is often greatly modified when these are in the form of very fine powders, or droplets, or threads, or films. It is still more surprising to find that the properties often depend more upon the fineness of division than upon the chemical composition of the material.

Colloidal state; colloidal systems. The particles in which we are now most interested are much too small to be seen by the most powerful ordinary microscopes; yet each particle is made up of many molecules, except in the case of such compounds as the proteins, the molecules of which are comparatively very large. Such particles, suspended in a liquid (or gas), constitute a *colloidal system.* The particles are said to be in a *colloidal state* and *dispersed* through the liquid (or gas). We speak of the small particles as the *dispersed phase,* and the liquid as the *dispersing phase.* The term *colloidal solution* is sometimes used, but the particles are not really in solution.

Colloid chemistry may be defined as the chemistry of very small particles, droplets, threads, and films.

How large are colloidal particles? In measuring the size of colloidal particles, all the common units of length are too large. So chemists have adopted much smaller units, namely the *micron* (μ), which is one thousandth of a millimeter, and the *millimicron* ($m\mu$), which is one millionth of a millimeter. In a general way it may be said that colloidal particles lie between 1 and 100 millimicrons in diameter. Some idea may be had of this size from the length of the following line, which is 10 cm in length:



$$10 \text{ cm} = 100 \text{ mm} = 100{,}000\ \mu = 100{,}000{,}000 \text{ m}\mu$$

How important is colloid chemistry? At first thought it might seem that this subject is of little importance. As a matter of fact it includes the chemistry of so many important materials that Bancroft calls colloid chemistry "the chemistry of everyday life." Here are some examples of the large number of materials whose composition and manufacture cannot be thoroughly understood without a knowledge of colloid chemistry: cement and porcelain; soaps; paints and lacquers; inks; rubber; dairy products of all kinds; water purification and sewage disposal; photography. Also, much of the matter that makes up living organisms, including our own bodies, is in a colloidal state.

How we can tell the difference between a suspension, a solution, and a colloidal system. Suppose we powder a solid and stir it in a liquid. How can we tell whether a suspension is formed, or a colloidal system, or a true solution? If the solid particles are simply suspended in the liquid, they are plainly visible to the naked eye or through a microscope and can be filtered out; but if they form either a colloidal system or a true solution, the particles are invisible even with a good microscope. To distinguish between the two, we make use of the *ultramicroscope* or, more commonly, of the *Tyndall effect*, named after the great English scientist who devised it.

The Tyndall effect. The air in a quiet room always contains particles of colloidal size that are too small to be seen as objects by a good microscope. But if the room is darkened and a beam of sunshine comes in through a small hole, these minute particles can be seen as bright, flashing points, or motes, dancing in the sunbeam. In like manner a colloidal dispersion in a liquid that appears perfectly clear to the eye, even when viewed through an ordinary microscope, is seen to be full of moving particles when a strong beam of light shines through the liquid (Fig. 296). This bright path of light through the liquid, as seen in Fig. 296, is called **the** *Tyndall effect.* A true solution shows no Tyndall effect.

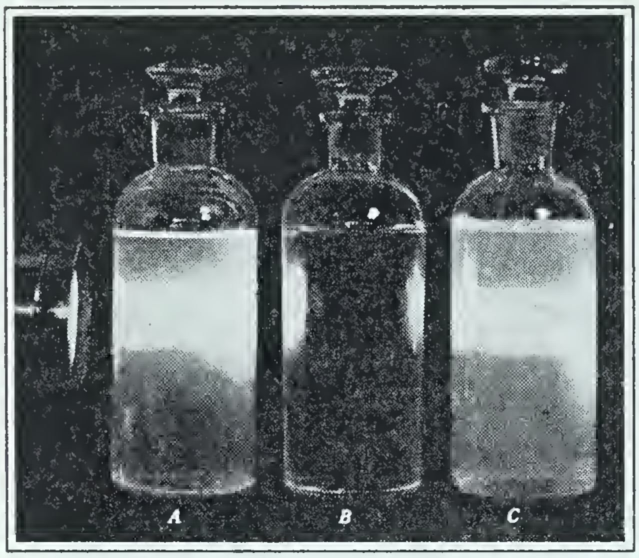


FIG. 296. The Tyndall effect

Light from a lantern is directed through the three bottles *A*, *B*, and *C*. *A* and *C* contain colloidal dispersions, and *B* a true solution

The ultramicroscope. An instrument which greatly magnifies the Tyndall effect is the ultramicroscope. A strong beam of light is directed through the liquid, which is viewed through a microscope that is mounted at right angles to the beam. Any colloidal particles that may be in the liquid are perceived not as *objects* but as bright specks of light moving about in all sorts of ways (Fig. 297).

The Brownian movement. The cause of this dance of particles, known as the *Brownian movement*, was a mystery for a long time, but now we know it is due to the never-ceasing motion of the molecules of the liquid. These are moving with high velocity, and constantly bombard the solid particles. The botanist Brown discovered this motion.

How colloidal dispersions are made. There are two general plans for making colloidal dispersions, each of which may be modified in many details:

1. An insoluble solid may be powdered to the necessary fineness and then stirred into the liquid (usually water). Special colloid mills are now made for grinding materials into this fine form.

A colloidal dispersion of gold, silver, or platinum is easily made by forming an electric arc between two wires of the metal dipped under water. The current tears off minute particles as a kind of smoke and disperses them through the water (Fig. 298).

2. We may bring about a reaction that ordinarily causes a precipitate but under such conditions that the minute particles first formed fail to collect into particles large enough to settle as a precipitate.

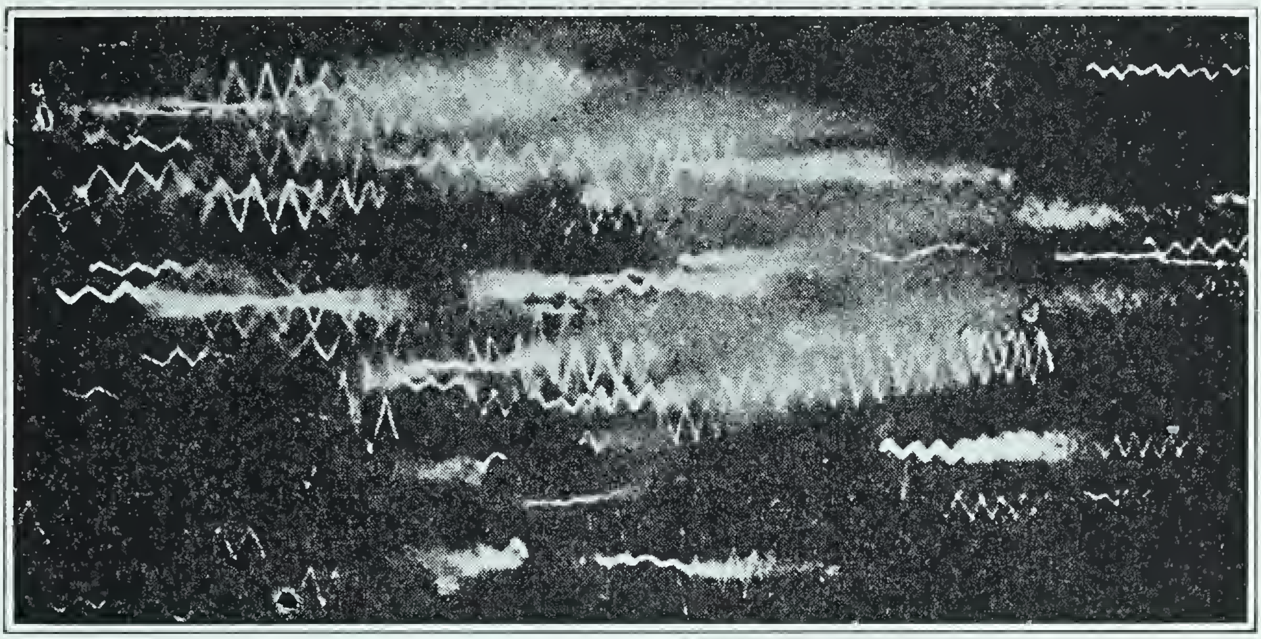


FIG. 297. Photograph made by attaching a camera to an ultramicroscope, showing movement of colloidal particles

Courtesy of Dr. P. V. Wells and Dr. Ross A. Gortner

For example, we may add acid to a dilute solution of the salt called sodium thiosulfate. No immediate precipitate of sulfur forms; but colloidal sulfur is present, as is evident from the white color.

Properties of colloidal dispersions. Most of the properties of colloidal dispersions are due to the size of the particles rather than to the kind of matter composing them.

1. All colloidal particles are charged electrically, some kinds positively and some negatively. In an electrical field these particles are attracted to one or the other electrode.

2. Many colloidal dispersions are highly colored, but the color gives us little clue as to what is present. Colloidal gold may be red, blue, green, or violet, depending upon the size and uniformity of the particles. A little ferric chloride added to boiling water gives a deep-red colloidal iron hydroxide.

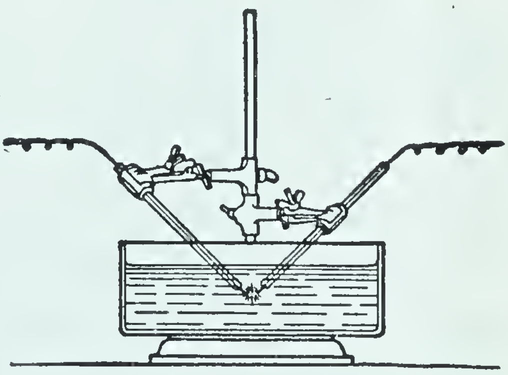
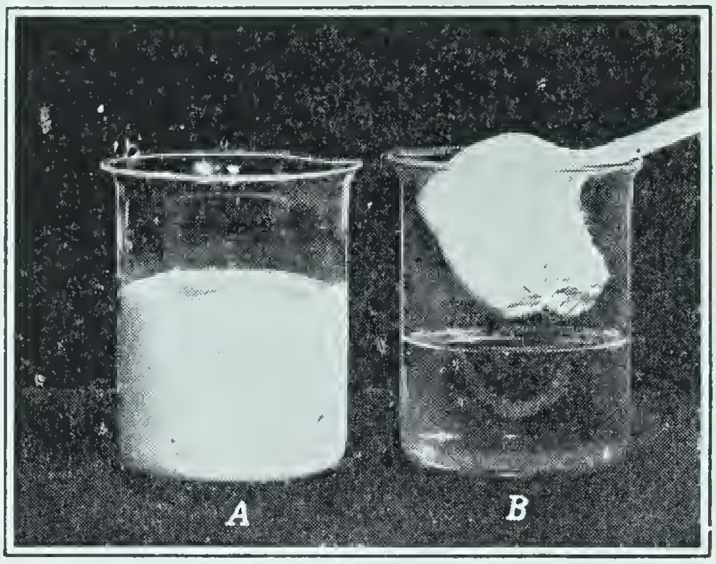


FIG. 298. Preparing metallic colloidal dispersions by sparking under water

It takes very little of the colloidal substance to make an intense color. A few milligrams of gold will color a liter of water. A very little of the element selenium added to glass makes the intensely red glass of the automobile taillight.



The beaker *A* contains the sap (latex) of the rubber tree, which consists of a colloidal dispersion of rubber. While the latex has many uses, for most purposes the rubber and not the dispersion is desired. To obtain this, a small percentage of acetic acid is added to the latex and the mixture is then stirred with a rod. The rubber particles coagulate and cling to the rod as shown in *B*

FIG. 299. The coagulation of a colloidal dispersion by an acid

Many colored glasses and glazes owe their color to colloidal material of various sorts, and many gems are colored in the same way.

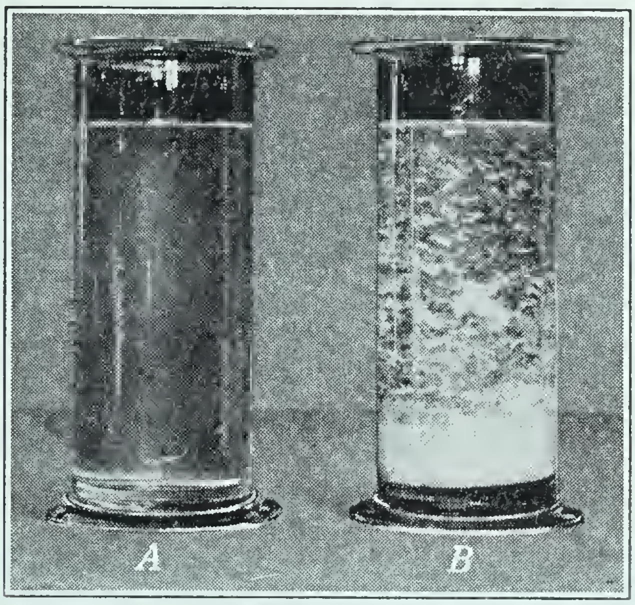
3. Since the colloidal particles are exceedingly small, they cannot be filtered out by an ordinary filter.

Coagulation of colloidal dispersions. It often happens that a colloidal dispersion is not suited to our needs, and we want to recover the colloidal material. We must then change the electrical or chemical conditions so that the very small particles will grow together into large clumps that will precipitate. There are a number of ways to bring this about.

1. A given substance may tend to remain dispersed in an *alkaline* solution, but to be precipitated in an *acid* solution; or it may be just the reverse. So the addition of a little acid or alkali is apt to cause the colloidal particles to precipitate, or *coagulate*, as it is called.

For example, casein, colloidally dispersed in milk, coagulates to a curd when the milk becomes sour or acid in reaction. Rubber is coagulated from the sap of rubber trees by the addition of acetic acid (Fig. 299). On the other hand, many metallic oxides are precipitated by alkalies.

2. Sometimes a concentrated salt solution will coagulate a colloidal dispersion. Thus, most river water carries much colloidal clay and organic matter. When it reaches the salt water of the ocean, this matter is precipitated and builds up



The cylinder *A* contains a colloidal dispersion of soap. The cylinder *B* shows the result of adding a saturated solution of sodium chloride to the soap dispersion. The particles coagulate and soon precipitate. Later, we shall see that advantage is taken of this reaction in the manufacture of soap

Fig. 300. The coagulation of a colloidal dispersion by a salt

the great river deltas, such as those of the Mississippi or the Nile. In every soap factory colloidal soap is separated from its solutions by the addition of common salt (Fig. 300).

3. We have seen that all colloidal particles are electrically charged. It has been found that when two colloidal dispersions of opposite charge are brought together, they precipitate each other. For example, in ordinary water purification the negative colloidal particles in river water are precipitated by the positive colloids supplied by alum or iron salts added for that purpose. The processes of dyeing and tanning depend upon this same principle.

Preserving a colloidal dispersion. In industrial operations it often happens that we want to preserve, or *stabilize*, the colloidal state. One way to do this is to reverse the acidity or alkalinity that caused the coagulation. To illustrate, antimony sulfide precipitated in acid solution may be dispersed again in an alkaline medium. Sometimes we may filter the precipitate from the salt solution that produced precipitation and disperse it once more in pure water.

If we bring together two colloids of the same electrical sign, each tends to hold the other in colloidal state. This is why we add gum arabic to some kinds of ink to hold the colloidal black material in dispersion; or dextrin, starch, or gums to many industrial and medicinal preparations.

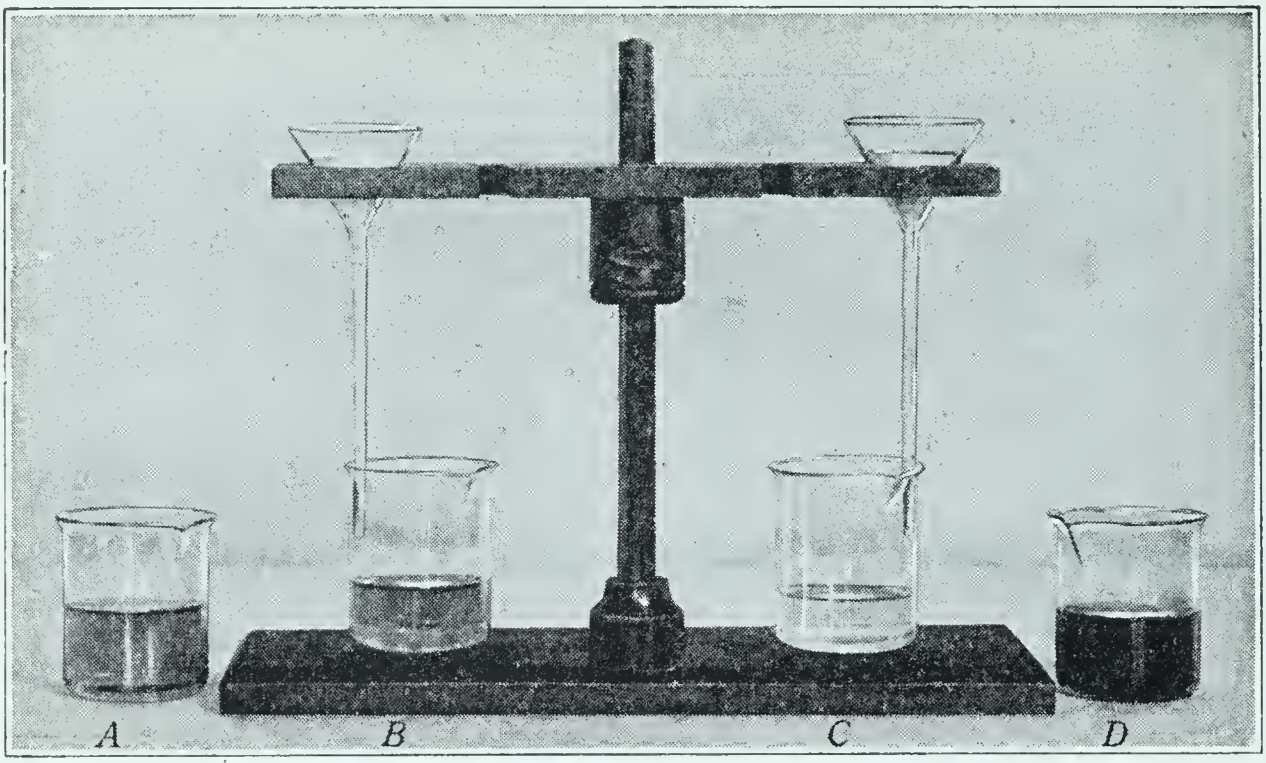


Fig. 301. Removing coloring matter by adsorption

The coloring matter in solution *A* passes through the filter (see filtrate *B*). If we add some boneblack to the solution (beaker *D*), stir the mixture, and heat it, the boneblack adsorbs the coloring matter. If now we filter the mixture, the filtrate is colorless, as shown in *C*

Colloids and crystallization. It is an interesting fact that the presence of a colloidal material in a solution often tends to prevent distinct crystallization of the solute, or at least to make the crystals very small and soft. So we put colloidal gelatin into ice cream, and gelatin, starch, dextrin, and similar materials into many candies, and into electrolytic baths during electroplating; for in these processes we wish to avoid large or hard crystals. The colloidal materials in honey keep the concentrated sugar solution from crystallizing.

Various kinds of colloidal dispersions. So far we have been thinking almost entirely of dispersions of solids in liquids. As might be expected, we may have other states of matter dispersed in each other. We may have a gas dispersed in a liquid, as in carbonated waters and ginger ale; or a gas dispersed in a solid, as in soaps that float on water. We may have a liquid dispersed in a gas (clouds) or in another liquid (as in cream, which consists of butterfat dispersed in water). We have solids dispersed not only in liquids, as in the case of colloidal gold, but also in gases (smoke), as well as in other solids, as is the coloring matter in glass and gems.

Adsorption. Sometimes a solid can be got in a very porous condition that has a large total surface in comparison with its weight. Activated charcoal (p. 144) is a solid of this kind, and it is estimated that 1 ml of it has a surface of 1000 sq m. Such materials (as well as colloidal particles whose surface is proportionally much greater) often have the property of attracting, or *adsorbing*, gases or dissolved substances from their solution.

At room temperatures 1 ml of activated charcoal will adsorb about 150 ml of ammonia gas. It is this property that makes activated charcoal valuable in gas masks. It will also adsorb gasoline molecules from natural gas; and this is one of the ways by which we increase our gasoline supplies. Boneblack will adsorb certain coloring matters from their solution (Fig. 301). By its use we may remove the coloring matter from crude sugars and so obtain a snow-white product. Fuller's earth is a kind of porous clay used for removing colors in refining oils such as cottonseed oil. It is evident from these examples that this property of adsorption is of wide use in chemical manufacturing.

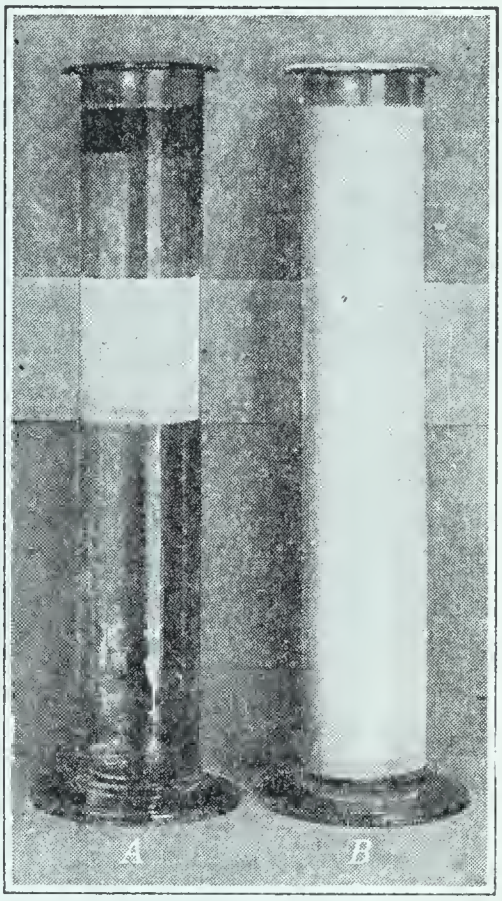


FIG. 302. Emulsions

When oil and water are shaken together, the oil soon separates on standing (*A*); if a little soap is added to the oil and water, and the mixture shaken, the emulsion becomes more permanent (*B*)

Emulsions. If we pour together two liquids that do not mix, like oil and water, and shake the mixture vigorously, we get a milky-looking fluid called an *emulsion* (Fig. 302). This consists of very minute drops of the one liquid dispersed through the other. If we let an emulsion of oil and water stand, it will very soon separate into the two liquids, the oil floating on the water.

Emulsifying agents. To make an emulsion of any kind *permanent*, we must add a third colloidal substance insoluble in both of the liquids. This is called the *emulsifying agent.* It seems to form a little skin over the surface of the drops and prevent them from running together into big ones. *Milk* is an emulsion of butterfat in water, with *casein* as the emulsifying agent. When the milk turns sour, the casein coagulates, and the butterfat is then easily collected into large lumps of butter.

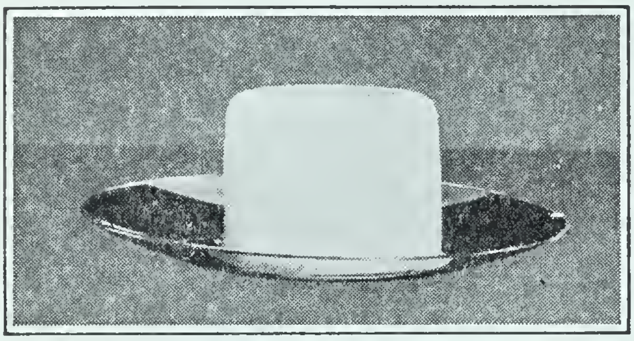


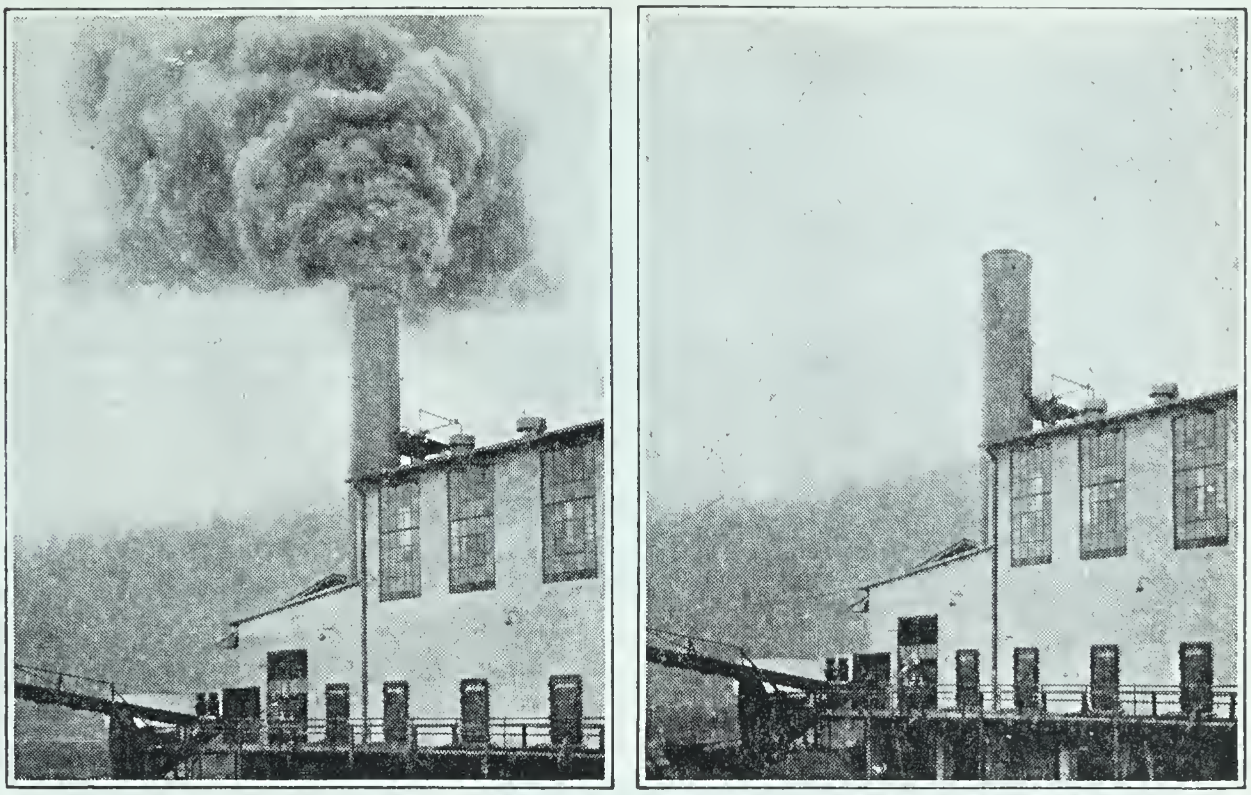
FIG. 303. Silicic acid in the form of a gel

Most of our common disinfectants owe their properties to cresylic acid (p. 487) emulsified in water, with a small percentage of soap as the emulsifying agent. In *mayonnaise,* olive oil is emulsified in water (usually with a little vinegar added) by the colloidal yolk of egg, forming a stiff, almost jellylike product. Fluids that form the webs of spiders and silkworms are secreted as emulsions which almost at once dry to form very fine filaments.

Jellies. Sometimes a colloidal substance takes the shape of very thin films rather than particles or filaments, and these films may form in such a way as to enclose the liquid, much as the walls of the honeycomb enclose the honey or as the pores of a sponge hold water. When this happens the dispersion may *set* to a more or less firm form called a *jelly* or *gel.* If we add acid to a solution of sodium silicate, the dilute dispersion of silicic acid soon sets to a firm jelly (Fig. 303).

In fruit jellies it is a substance in the unripe fruit called *pectin* that makes the supporting structure. In gelatin or glue the jelly may be dried out to a very compact form; but when this is dissolved in hot water and cooled, it once more sets to a jelly. Soap is a partially dried jelly; many minerals, such as agate, flint, and opal, are dried jellies; photographic films and many high explosives are jellies.

Smokes. Evidently we may have very fine particles dispersed in the air rather than in water, and such a dispersion is a *smoke.* It is often very hard to condense the particles of a smoke into solid form, and this fact is of enormous industrial importance. Many precious materials literally "go up



Western Precipitation Company

A *B*

FIG. 304. The effect of the Cottrell method for abating dust and smoke

A shows a factory not equipped with any device for abating dust and smoke. *B* shows the same factory after equipment with the Cottrell apparatus

in smoke" from the stacks of smelters. Much zinc is lost as a smoke of zinc oxide in brass foundries. Valuable potassium compounds are lost in the smoke of cement burners. Ordinary carbon smoke causes great losses to the individual, though profit to the laundries.

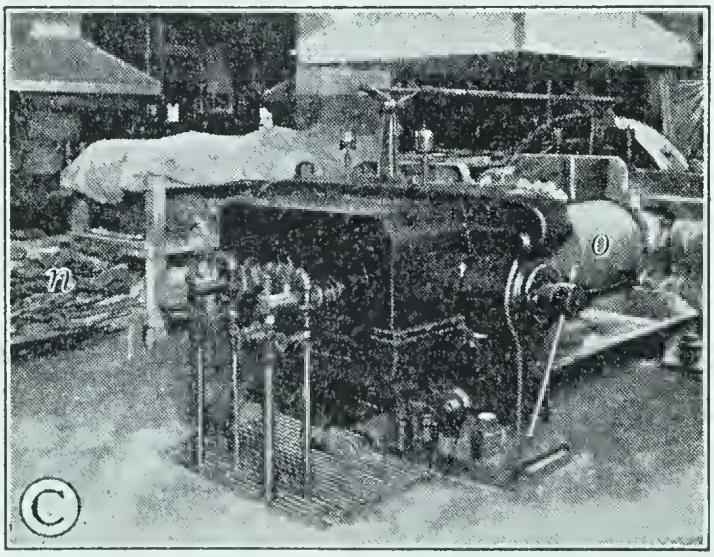
The Cottrell process. All these smoke particles are electrically charged. This fact led the American chemist Cottrell to invent a most effective process (Fig. 304) for the recovery of these particles by causing the smoke to move past metal plates and points charged electrically. The smoke particles lose their charge and then coagulate, much as a precipitate forms from a solution. They settle to the bottom of the chimney and may be recovered if desired.

SOME INDUSTRIAL MATERIALS, COLLOIDAL IN CHARACTER

Rubber — where we get it. Everyone knows that Columbus discovered America, but most of us will be quite surprised to learn that he discovered rubber also. While on his second voyage he found the children in South America

The rubber is obtained from rubber trees by tapping. The rubber, in the form of an emulsion, flows from the trees and is collected in cups and buckets, as shown in A. This emulsion resembles milk in appearance and is known as the *latex*

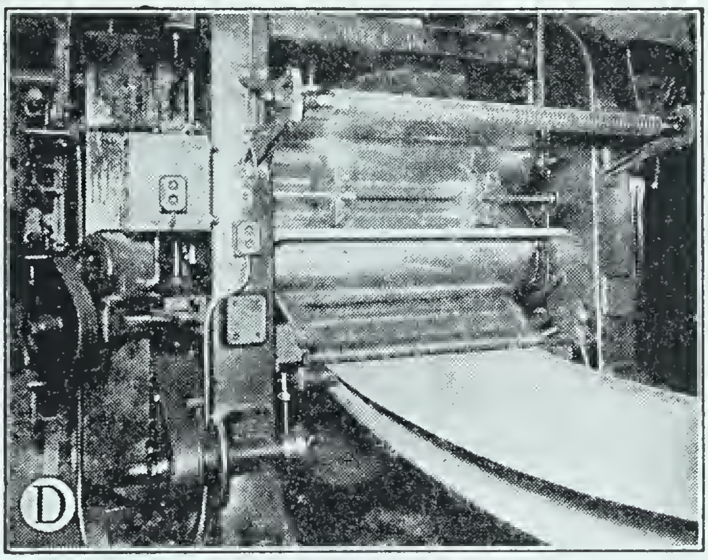
The rubber is obtained from the emulsion by coagulating it with acetic acid (Fig. 299). Formerly it was obtained in a more primitive way by pouring the emulsion, a little at a time, over the end of a stick and evaporating the water over a fire, as shown in B



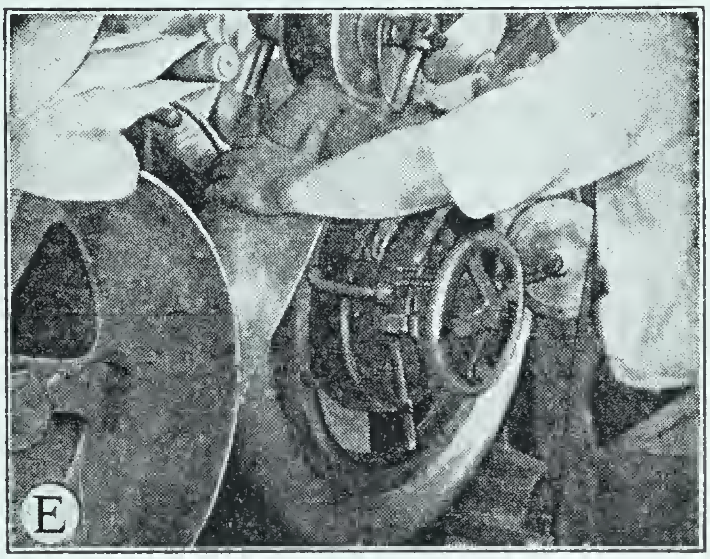
The raw rubber is next mixed (or compounded) with sulfur and certain substances such as zinc oxide and carbon black. This is done by running the materials between large revolving cylinders (*O*), as shown in C, until thoroughly mixed. Piles of the raw rubber are shown marked ***n***

Fig. 305. A, B, C. Some steps in the manufacture of automobile tire casings

In D cotton fabric is being impregnated with the compounded rubber by running the fabric and the rubber between large cylinders of metal. In cord tires the cord is wrapped about the core, and the cord as well as the interstices is filled with rubber



The method of building up the casing varies with the size and kind of tire desired. One method consists in winding the rubberized fabric on an iron wheel, the surface of which is the shape of the inner surface of the desired casing. Another method consists in building the casing flat by winding it on a flat drum, then forcing it into the desired shape



The tire casing is then placed in a mold, as shown in F, and heated in large steam ovens. In this process the rubber is vulcanized and toughened. It is then removed, and the finishing touches are given it

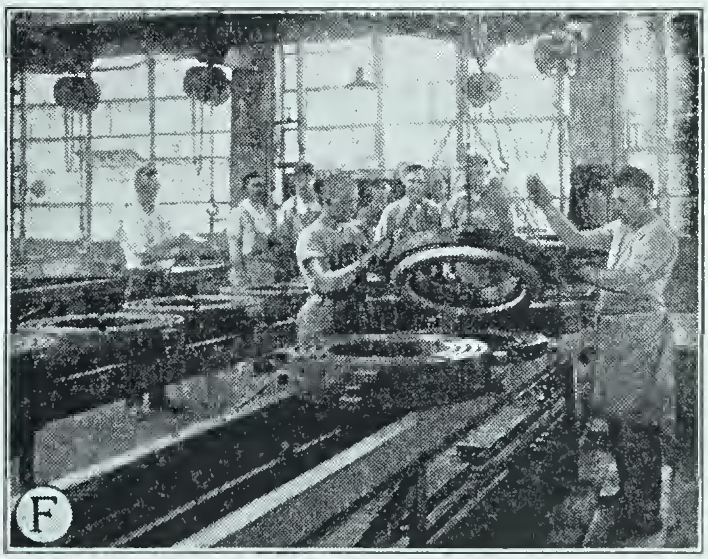


Fig. 305, D, E, F. Some steps in the manufacture of automobile tire casings playing with balls made of a dark material. He was at once greatly interested in these balls that would bounce into the air when thrown on the ground. But nothing came of this discovery for a long time, for there was no demand for a material of this kind.

When the invention of bicycles created a demand for wheels with cushioned rims, and, later on, automobiles could not do without them, rubber came into its own, and the researches set up in all sorts of laboratories quickly found countless other uses for it.

Rubber is got from the rubber tree, of which there are many species. These trees grow wild in parts of South America. Large plantations, amounting to several millions of acres, have been developed in Java, Sumatra, Ceylon, the Malay States, and other tropical regions. At the present time practically our entire supply of rubber comes from these plantations. Its formula is an unknown multiple of the simple formula C_5H_8 and is written $(C_5H_8)_x$. Products that are similar to natural rubber can be made in the laboratory, but they are more expensive.

How we get rubber from the trees. Rubber is obtained from rubber trees by *tapping*, or cutting nearly through the bark. A milky fluid exudes from these cuts and is collected in cups, as shown in Fig. 305, *A*. This fluid is called *latex*. It is a dispersion of minute rubber particles in water, protected from coagulation by a small percentage of nitrogenous matter. Latex looks like milk (Fig. 299, *A*) and is an emulsion. The rubber particles are dispersed in the latex, much as the butterfat is dispersed in milk. These rubber particles are present in great numbers. In his book on *The Reign of Rubber*, Geer states that if the particles in a gallon of latex were placed side by side, they would make a tiny rubber thread 372 miles long.

Rubber is separated from the latex by adding a small percentage of acetic acid, which destroys the emulsifying agent, allowing the rubber to separate in the form of a soft, light dough (Fig. 299, *B*). At present, some latex is being used without coagulation, especially in the making of certain grades of paper, artificial leather, and tires.

Goodyear's great discovery. Natural rubber is sticky and changes its properties with the temperature, becoming brittle when cold and like gum when hot. In this natural state it is nearly worthless for most purposes. About one hundred years ago the American inventor Goodyear (Fig. 306) made his great discovery. While trying to overcome the defects of rubber, he chanced to drop a mixture of rubber and sulfur on a hot stove and found that the product had all the desirable properties of rubber and few of its defects. This heating of rubber with sulfur has become a regular process called *vulcanization*, and we say that rubber so treated is *vulcanized*.

Fig. 306. Charles Goodyear (1800–1860)

The American inventor who discovered the method of vulcanizing rubber and so making it useful. (Courtesy of the Goodyear Tire and Rubber Company)

Most rubber articles are not pure rubber. For most purposes the pure rubber has to be mixed, or *compounded*, with other materials, called *fillers*. These give strength and other desired properties to the finished products. Carbon black and zinc oxide are among the most common of these fillers. A small percentage of certain organic compounds called *accelerators* is also added. These shorten the time required for vulcanization and add other desirable properties.

Rubber made in the laboratory. Many efforts have been made to synthesize natural rubber or products that have its essential properties. These efforts have been successful, and there are now being made a number of products, some of which are equal to natural rubber for tires and better for special purposes. They are known by various trade names, such as Buna, Neoprene, and Ameripol. As yet they are more expensive than natural rubber.

PLASTICS

Something about plastics. In its broadest sense the group of materials called plastics includes all those that can be worked or molded into some desired shape. It therefore includes such materials as cement and clay, which are made plastic by adding water; as well as glass, which becomes plastic when heated.

But in recent years the word *plastics* has been confined largely to products most of which are made from relatively simple organic compounds, and which have the property of becoming hard when heated. The finished products are complex in composition and are formed chiefly through the combination of many molecules of simpler compounds, — a process known as *polymerization.* Slosson likened the process to a financial merger, and said the plastic was a molecular trust formed by the combination of a large number of small molecules.

One of the first of these plastics that came into wide use is known as *bakelite*, named after its discoverer, the American chemist Baekeland. It is made by heating a mixture of formaldehyde (p. 470) and phenol (p. 487) under pressure. Like most other plastics of this general kind, it is hard, inactive, insoluble, noncrystalline, and a nonconductor of heat and electricity. So it lends itself to many uses (Fig. 307). In recent years literally hundreds of similar plastics have been put on the market under various trade names, and their uses are almost countless. One recently made is known by the trade name of *lucite.* It is clearer than optical glass, is only half as heavy, and is not brittle.

The discovery of these plastics is one of the greatest in the field of chemistry in recent years, and has even been likened in importance to the discovery of aniline dyes.

CHAPTER SUMMARY IN QUESTION FORM

1. Give the meaning of each of the following terms, and illustrate each by an example: (*a*) colloidal state; (*b*) colloidal dispersion; (*c*) colloidal system; (*d*) dispersed phase; (*e*) dispersing phase.

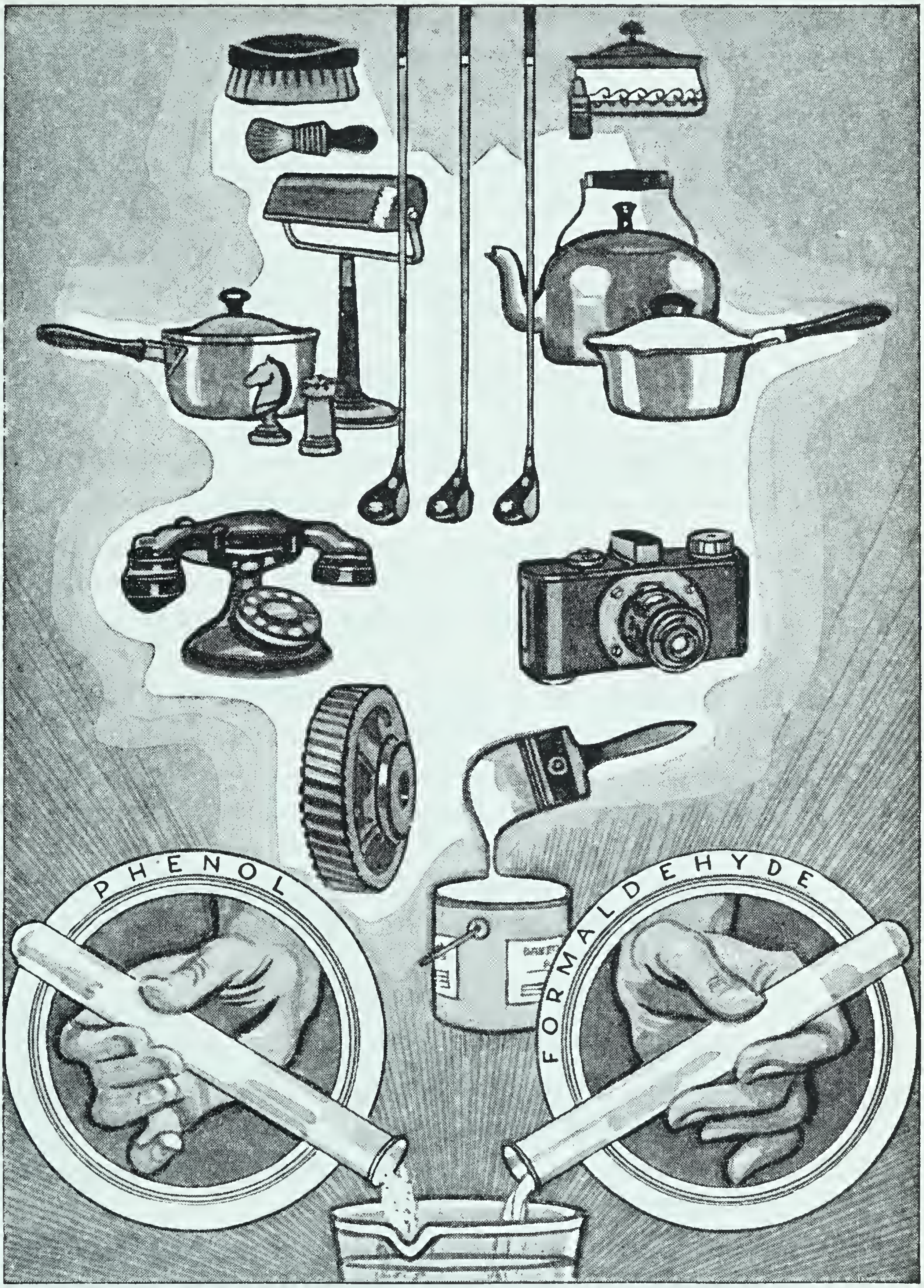


Fig. 307. This figure shows a number of articles, all or parts of which are made from plastics

Phenol (p. 487) and formaldehyde (p. 470), as well as a great many other chemicals, are used in the manufacture of plastics

2. (*a*) Define the term *colloid chemistry.* (*b*) Of what importance is this subject?

3. (*a*) What are the units of length used in colloid chemistry? (*b*) What are the limits of the diameters of colloidal particles?

4. How can you tell the difference between a suspension, a solution, and a colloidal system?

5. (*a*) What is meant by the Tyndall effect? (*b*) What does it enable one to do?

6. (*a*) Why do not colloidal particles precipitate? (*b*) Describe an experiment which shows that the molecules in a liquid are in rapid motion.

7. Mention two ways in which matter can be obtained in the colloidal state.

8. Mention three characteristics of colloidal dispersions.

9. In what way do colloidal particles resemble ions?

10. Should you say that the color of a colloidal dispersion depends essentially upon the size of the particles, the uniformity of the particles, the materials used, or the nature of the electrical charge?

11. What operation will remove precipitates from a liquid but will not remove colloidal particles?

12. Suppose you have a colloidal dispersion, and wish to precipitate (coagulate) the particles so as to remove them from the liquid. What three methods could you try?

13. (*a*) Mention two industrial operations whose success depends on preserving the colloidal state. (*b*) How can you preserve the colloidal state?

14. Activated charcoal adsorbs large volumes of certain gases. What is the meaning of the term *adsorb* as used in this connection?

15. In addition to charcoal, mention two other good adsorbing agents and tell for what each is used.

16. What substance causes the colloidal dispersion that exists in fruit juices to form a jelly, or *gel*?

17. (*a*) What property of colloidal particles makes possible the Cottrell process for preventing smoke? (*b*) Describe the process.

18. Discuss the subject of rubber under the following heads: (*a*) its source; (*b*) the separation of the rubber from the latex; (*c*) vulcanizing; (*d*) composition; (*e*) fillers.

19. What materials are included under the word *plastic*? Give an example of a plastic and name some of the objects made from it.

THOUGHT QUESTIONS

1. Crank-case oil and oil used in other machinery become very black; yet little of the color is removed by filtration. How do you account for this?

2. Sugar is used in making jelly. Ordinarily the sugar does not crystallize out when the jelly forms, although an occasional glass is found with large crystals of sugar scattered through the jelly. Explain.

3. Fertile soils are essentially a kind of colloid jelly made up of clay and organic matter. When soluble salts such as ammonium sulfate and sodium nitrate are used as fertilizers, why are they not all dissolved and carried away by the first rain?

4. Can you explain why gravity, which causes large particles suspended in a liquid to settle, will not also cause small particles to settle?

5. From your knowledge of colloidal dispersions, give a reason for each of the following: (*a*) the formation of large soil deposits at the mouth of certain rivers that empty into the ocean; (*b*) the use of gums in the manufacture of some inks; (*c*) the use of gelatin in the manufacture of ice cream; (*d*) the use of the yolk of egg in making mayonnaise.

OPTIONAL EXERCISES

1. Arrange the necessary apparatus for showing the Tyndall effect, using an ordinary projection lantern or any other source of a strong beam of light. Test different liquids before the class, showing in this way which are true solutions and which are colloidal dispersions.

2. Collect for your school museum a set of samples of the various substances that are used in making rubber tires (dealers in tires will help you to procure samples of pure rubber).

UNIT READINGS

BANCROFT. *Applied Colloid Chemistry.* [This book covers the whole field of colloid chemistry in an interesting way and is good for general reading on the subject.]

BEERY. *Stuff.* [Pages 205–213 tell of rubber.]

CLARKE. *Marvels of Modern Chemistry.* [Chapter VIII is entitled "Colloids — the World of Neglected Dimensions." Chapter XVII deals with sand and clay.]

DARROW. *The Story of Chemistry.* [Chapter VIII treats interestingly of rubber, and Chapter IX of colloids.]

Fisher. "Natural and Synthetic Rubbers," *Journal of Chemical Education*, Vol. XIX, pp. 522–530. [An up-to-date discussion of this important subject.]

Fisher. *Rubber and Its Uses.* [An interesting book of one hundred and twenty-eight pages.]

Foster. *The Romance of Chemistry.* [Read Chapter XIX, "The A–B–C of Pottery and Glass," and Chapter XX, "Colloid Chemistry."]

Harrison. "More Precious than Rubies," *Harper's Magazine*, Vol. 175 (November, 1937), pp. 635–642. [A most interesting article on glass.]

Holmes. *Out of the Test Tube.* [Chapter XVIII, entitled "Windows toward Heaven," tells a brief and interesting story about glass.]

Howard. "Agates," *Journal of Chemical Education*, Vol. X, pp. 67–70.

Howard. "Opals," *Journal of Chemical Education*, Vol. XIII, pp. 553–556. [A good and well-illustrated article.]

Ryan. "The Story of Portland Cement," *Journal of Chemical Education*, Vol. VI, pp. 1855–1868 and 2128–2146. [Interesting; many pictures.]

Slosson. *Creative Chemistry.* [Chapter VIII, "The Race for Rubber," is very good, especially from a historical standpoint. Chapter VII, "Plastics," is excellent but not up to date.]

Weeks. *The Discovery of the Elements.* [Read of the discovery of silicon, pp. 162, 163; also of the discovery of boron, pp. 156–161.]

The Science Leaflet. [No. 16 of recent volumes tells about the silicon and boron families; No. 17 treats of colloids; No. 13 of Vol. XI contains an excellent discussion of plastics and of rubber.]

The World Book Encyclopedia. [This work contains well-illustrated articles on cement, glass, porcelain, pottery, and rubber.]

Note. The Corning Glass Works, Corning, New York, publishes a booklet entitled *A Short Story of Technical Glassware*, which is offered gratis to students of chemistry. The booklet is very interesting and contains many pictures of glass-making.

Unit Ten. The Chemistry of Fuels

THIS unit deals chiefly with petroleum and coal — the energy they give us, and the things we get from them. Of course, in times past there have been civilizations that have had neither petroleum nor coal. Egypt was such a country, and until rather recent years China was another. Neither of them had even much wood for fuel; for they had used up all their forests.

But here in America can you imagine cities without gas or electric lights; highways without automobiles or filling stations; landing-places without airplanes; engines (on railways or in factories and power plants) without coal? Could we endure our climate with no means of heat (for what forests we have would all be gone in a few years)? Could we get along without metals? Practically all these metals require coal as a reducing agent in getting the metals from their ores, and as a source of power to run the engines that fashion the metals into useful forms.

Perhaps we have thought of all these things. But few people realize how many of our necessities come indirectly from petroleum or coal. We need to remember the solvents that make possible such things as rayon and cellophane; the materials that make our many resins, lacquers, and plastics; the dyes and drugs that make life colorful or relieve illness. Most of these things we shall study in the next unit.

In this unit we shall limit our attention to the direct importance of petroleum, natural gas, coal, and the varieties of fuels that can be got from any of these.

CHAPTER XXXVII

Petroleum—A Magical Fluid

[Next to Water the World's Most Important Liquid]

What is petroleum? Everyone can name the most important and abundant liquid in this world. If one were to ask, "What liquid comes second in importance?" the answer might not be so prompt, but all would finally agree that it is petroleum, a dark-colored liquid found in large quantities in many places throughout the world. In a few cases it comes to the surface of the earth as water does in artesian wells or springs. More often it is got by drilling wells into the natural supplies deep in the earth and pumping it to the surface.

Why is petroleum so useful? Of course, we could get along without petroleum; for we did so until comparatively recent times. But when large quantities of it were discovered, people became interested in it and found some simple uses for it. As time went on, its uses increased until today it runs our automobiles (about twenty-five million of them in the United States, or one to every five persons), lubricates our machinery, drives many of our ships and locomotives, flies our airplanes, plows our land and reaps our crops, heats and lights many of our homes, and in numberless other ways contributes to our present way of living.

The first to use petroleum. The people of northwest Persia burned petroleum for fireworks to entertain Alexander the Great. The Iroquois prized it as a medicine. The first to market it in modern times, or one of the first, was a Pittsburgh druggist who, in 1849, collected some of it from a salt well and sold it at fifty cents a half-pint bottle as "a natural remedy celebrated for its wonderful curative properties, procured from a well in Allegheny County, Pennsylvania."

The increasing output of petroleum. The fact that petroleum would burn suggested its use as a fuel and for lighting our homes. Since the amount collected from springs and salt wells was limited, it was proposed to get larger supplies by drilling deeper wells; and the first one drilled for the

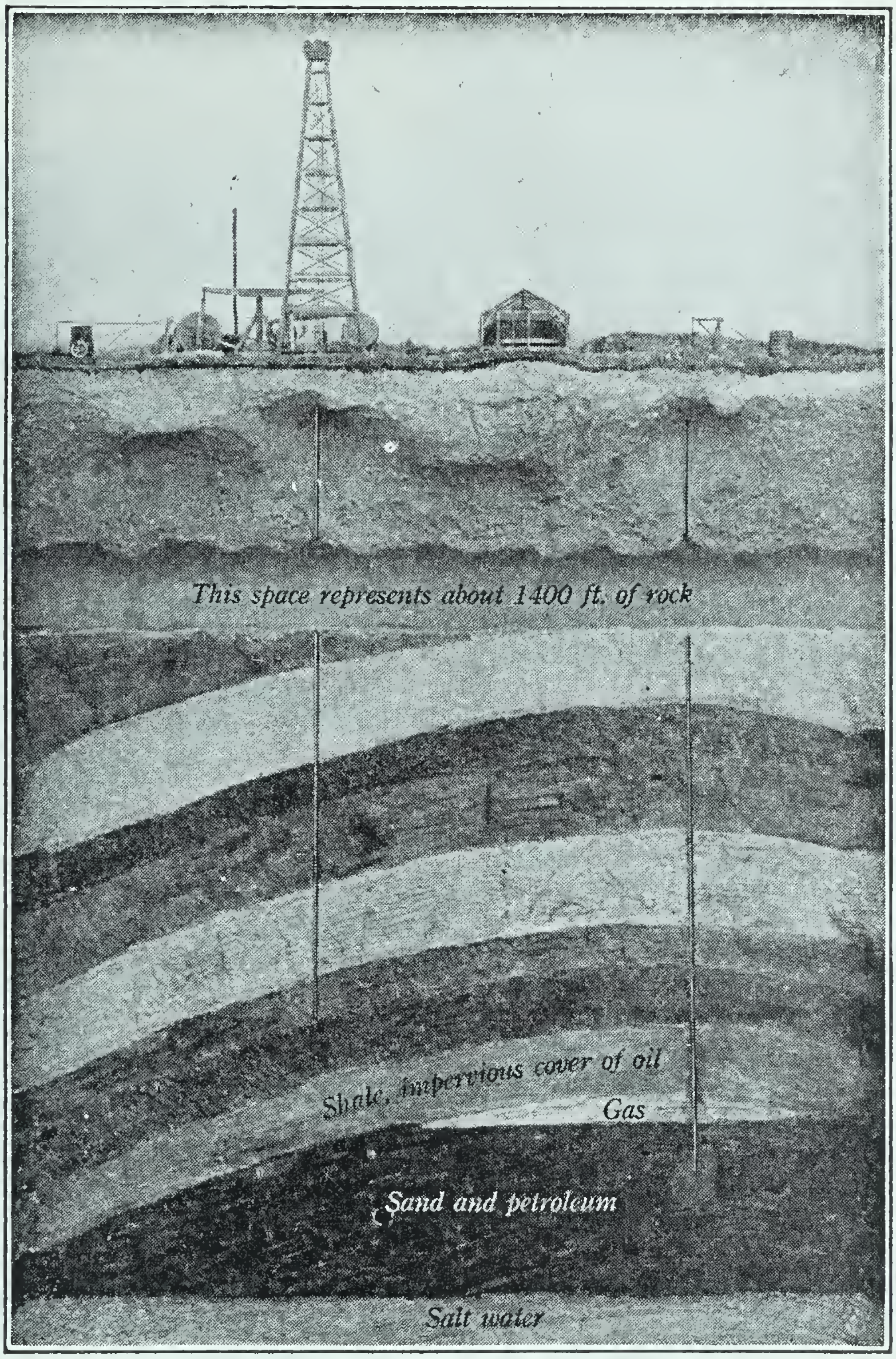

This space represents about 1400 ft. of rock
Shale, impervious cover of oil
Gas
Sand and petroleum
Salt water

FIG. 308. Typical structure of rocks in oil fields

Wells are sunk into the oil-bearing strata which occur at depths below the earth's surface varying from a few feet to 5000 ft or more. At the left of the picture the shaft is shown as having reached nearly to the shale which forms an impervious cover over the oil-bearing rock. On the right the shaft is shown as having penetrated into the oil-bearing rock, so that the oil can be pumped to the surface. Often the oil will flow to the surface under its own pressure. (Courtesy of the Field Museum of Natural History)

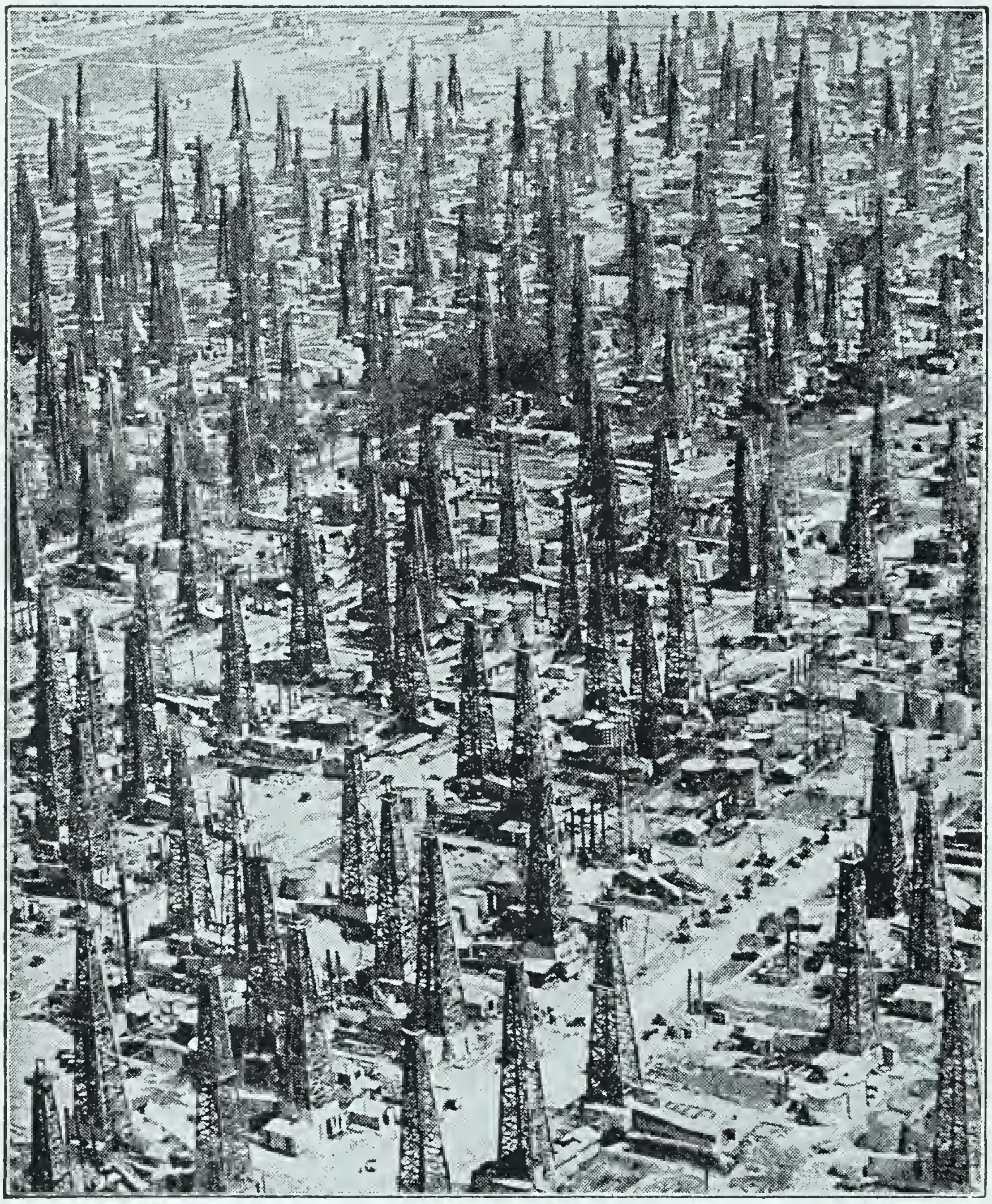


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Fig. 309. View in a typical oil field

A part of one of America's richest oil fields, namely the one located at Signal Hill, near Long Beach, California. Derricks are as thick as trees in a forest. The oil is stored in the large tanks shown in the figure, or else piped directly to the refineries express purpose of getting petroleum was at Titusville, Pennsylvania, in 1859 (Fig. 310). From that time petroleum production has grown until (prior to the war) the United States produced yearly more than one billion barrels (42 gallons each), or about eight barrels for each inhabitant. The principal petroleum-producing states are Texas, California, and Oklahoma.

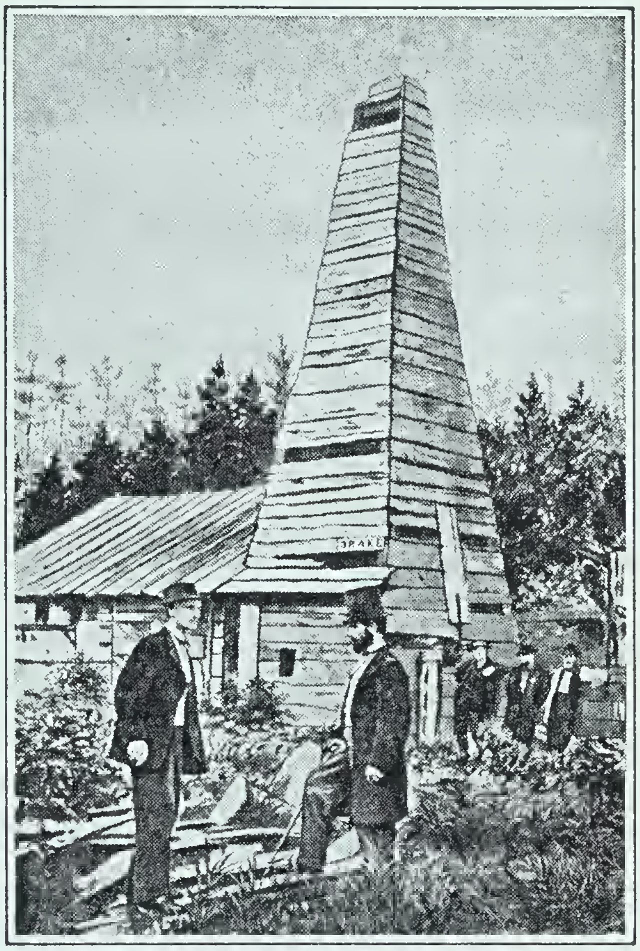


FIG. 310. The first oil well in the United States

This well was drilled by Colonel Drake at Titusville, Pennsylvania, in 1859. The well was 70 ft deep and furnished about fifteen barrels daily

Petroleum a mixture of compounds. Petroleum is a mixture of many compounds, the majority containing only carbon and hydrogen. *Any compound composed of carbon and hydrogen only is called a hydrocarbon.* There are many hundreds of these hydrocarbons; and, in order to simplify their study, chemists have arranged them in families, or series. The largest of these families, the *methane family* or *methane series,* is named from its first, or parent, member. In the following table are the names, formulas, and boiling points of the first eight members of this series. Others are known, up to those containing more than 30 carbon atoms.

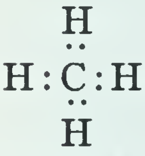
TABLE OF SOME HYDROCARBONS

NAME	BOILING POINT	NAME	BOILING POINT
Methane (CH_4)	− 161.4°	Pentane (C_5H_{12})	+ 36.2°
Ethane (C_2H_6)	− 88.3°	Hexane (C_6H_{14})	+ 69.0°
Propane (C_3H_8)	− 44.5°	Heptane (C_7H_{16})	+ 98.4°
Butane (C_4H_{10})	+ 0.6°	Octane (C_8H_{18})	+ 124.6°

(General formula C_nH_{2n+2}, in which n = the number of carbon atoms)

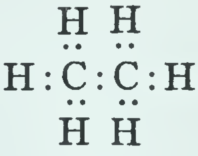
The table shows that each member of this series differs from the one before it by the group of atoms CH_2 and that the boiling points increase with the number of carbon atoms.

Why so many hydrocarbons? There are many hundreds of these hydrocarbons, and one naturally wonders why it is possible to have so many compounds of carbon and hydrogen only. The chief reason is that *carbon atoms can combine with each other*, forming increasingly long molecules. The carbon atoms in these molecules may be compared to the links in a chain, as shown in the structural formulas of the first four members of the series (valence electrons are represented by dots, p. 206):



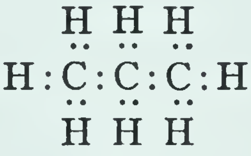
$$\begin{array}{c} \text{H} \\ \text{H}:\ddot{\underset{\cdot\cdot}{\text{C}}}:\text{H} \\ \text{H} \end{array}$$

Methane



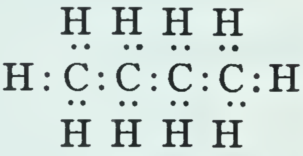
$$\begin{array}{c} \text{H}\ \text{H} \\ \text{H}:\ddot{\underset{\cdot\cdot}{\text{C}}}:\ddot{\underset{\cdot\cdot}{\text{C}}}:\text{H} \\ \text{H}\ \text{H} \end{array}$$

Ethane



$$\begin{array}{c} \text{H}\ \text{H}\ \text{H} \\ \text{H}:\ddot{\underset{\cdot\cdot}{\text{C}}}:\ddot{\underset{\cdot\cdot}{\text{C}}}:\ddot{\underset{\cdot\cdot}{\text{C}}}:\text{H} \\ \text{H}\ \text{H}\ \text{H} \end{array}$$

Propane



$$\begin{array}{c} \text{H}\ \text{H}\ \text{H}\ \text{H} \\ \text{H}:\ddot{\underset{\cdot\cdot}{\text{C}}}:\ddot{\underset{\cdot\cdot}{\text{C}}}:\ddot{\underset{\cdot\cdot}{\text{C}}}:\ddot{\underset{\cdot\cdot}{\text{C}}}:\text{H} \\ \text{H}\ \text{H}\ \text{H}\ \text{H} \end{array}$$

Butane

Properties of the hydrocarbons. By looking at the table (p. 429) it will be seen that the first four members of the series are gases at ordinary temperatures. Those containing from five to sixteen carbon atoms are liquids, the *boiling points* of which increase with the number of carbon atoms. Those containing more than sixteen carbon atoms are solids, the *melting points* of which increase with the number of carbon atoms. They are all insoluble in water and when pure are colorless. They are not readily acted upon by other compounds, even strong acids or bases having little or no action upon them. *All of them burn easily*, especially the gaseous and volatile liquid members of the series. When set on fire, the carbon burns to carbon dioxide, and the hydrogen to water.

How petroleum is "fractioned." Petroleum is made up of liquid hydrocarbons in which are dissolved both gaseous and solid hydrocarbons, together with many undesirable compounds. Before it can be used for most purposes, it must be distilled into "fractions," each fraction being composed of a mixture of compounds boiling between certain limits. Different forms of apparatus are used for doing this, many of them quite complicated; but the principle on which they all depend may be seen in Fig. 311. The crude oil is heated in large iron stills. Of course the compounds of lowest boiling points distill over first, gradually followed by others in the general order of their boiling points. The distillates boiling between certain limits of temperature are kept separate, since each fraction has a different use. The process just described is called *fractional distillation.*

Some petroleum fractions. The fraction composed of liquid hydrocarbons boiling from about 75° to 200° is called *naphtha*, which includes gasoline and benzine; that fraction boiling between about 200° and 300° is called *kerosene* (coal oil); the next fraction is used as a *fuel oil*; and, finally, there is a fraction composed of still higher-boiling hydrocarbons (some of them solid at ordinary temperatures) from which are obtained *lubricating oils*, *vaseline*, and *paraffin* (Fig. 313). A tarry residue left in the still serves as a paving and roofing material. A grade of coke is also obtained.

Refining the fractions. The different fractions obtained by distillation contain certain compounds that spoil their use and so must be removed. To do this each fraction is stirred separately, first with sulfuric acid, then with a solution of sodium hydroxide, and finally with water. It is then redistilled. *It is important to notice that none of these petroleum products are single compounds; each one is made up of a variety of compounds boiling between certain limits of temperature.*

Kerosene; gasoline. Formerly kerosene (coal oil) was the most valuable of the petroleum products; for it was the fuel in all the lamps our grandparents used. The lamp has given way almost entirely to the electric light; so the demand for kerosene has greatly diminished. With the coming of the automobile, kerosene gave way to gasoline as the most valuable of the petroleum products. Enormous supplies of gasoline are required to meet this new use, amounting (prewar) in the United States to about twenty billion gallons each year, or an average of about 180 gallons for each person.

Sources of gasoline. It was soon found that this huge quantity of gasoline could not be got by simply distilling petroleum in the usual way, and chemists tried to find means for increasing the yield. It was thought that, just as we may break a long chain into smaller lengths, so it might be possible to break the longer molecules that make up the higher-boiling hydrocarbons into the shorter molecules that compose the lower-boiling gasoline.

Experiments showed that this could be done. Different methods are used, but the chief one is the distilling of the higher-boiling oils at high temperatures and under pressure (Fig. 312). This is called the *cracking process.* By it the yield of gasoline from a given quantity of petroleum is increased two to three times. Strangely enough, the opposite process is now coming into use: the molecules of the gaseous hydrocarbons are joined together to make the low-boiling liquids that constitute gasoline.

Still further supplies of gasoline are also obtained from the natural gas that is usually found along with crude petroleum. This gas is chiefly methane, but it often contains vapors of the liquids that constitute gasoline. These vapors can readily be separated and liquefied. The resulting liquid is called *casinghead gasoline.*

The hydrogenation of coal. Recent experiments have shown that, under high pressure, hydrogen acts on powdered coal suspended in hot oil to make lubricating oils, gasoline, and similar products. This process is now in use in some foreign countries, and may come into use in our own country as our supplies of petroleum become exhausted.

The use of gasoline in our homes. Gasoline (or benzine, as it is often called) is a good solvent for fats and grease. So it is often used in our homes for cleaning fabrics of various kinds. But as it is very inflammable, and its vapor mixed with air is explosive, many deaths result from its household use.

MORE ABOUT THE HYDROCARBONS

Some single hydrocarbons. With few exceptions the products obtained by distilling petroleum, such as gasoline and kerosene, are mixtures of different hydrocarbons. But some individual hydrocarbons have special uses, and it is important to know something of the following: methane, ethylene, and acetylene.

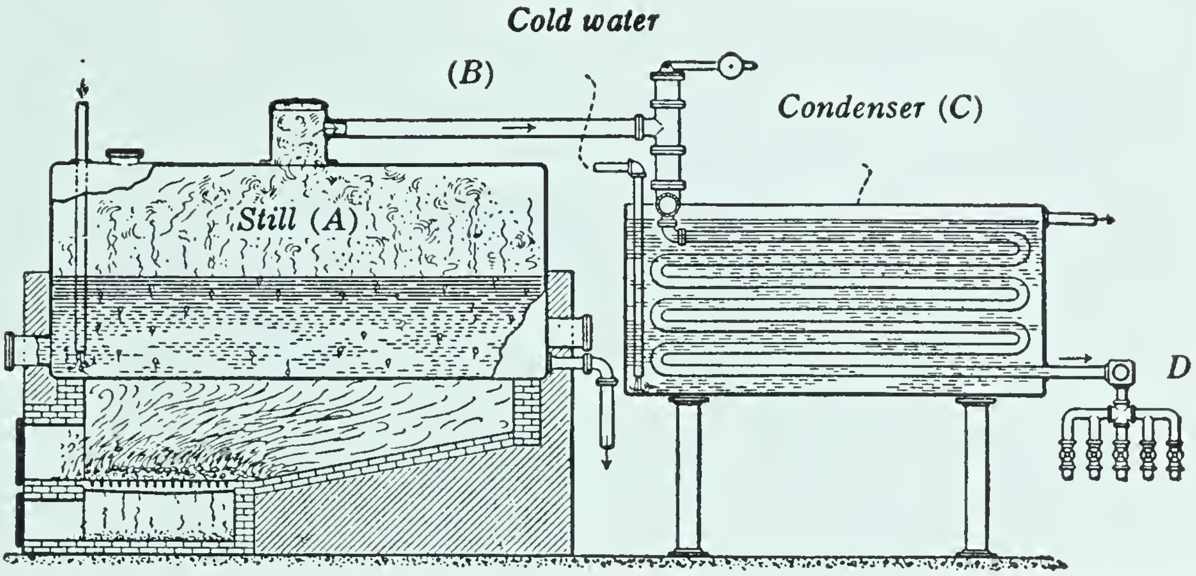


FIG. 311. Diagram of apparatus used for distilling petroleum

The crude oil is run into the large still *A* and heated. The vapors pass off through *B* and are condensed in *C*. The resulting liquids are drawn off through *D*

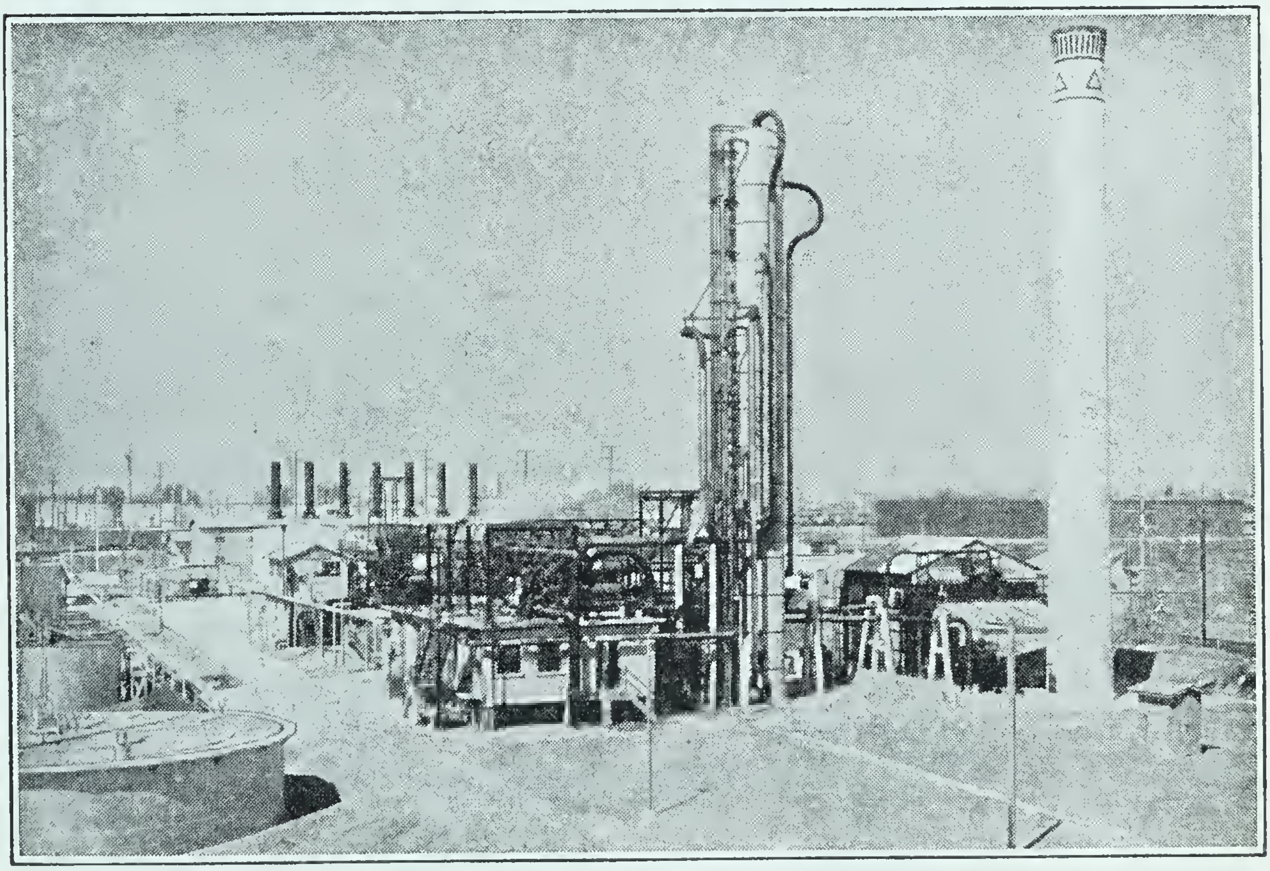


FIG. 312. View of a petroleum refinery, in which the yield of gasoline is greatly increased by the "cracking process"

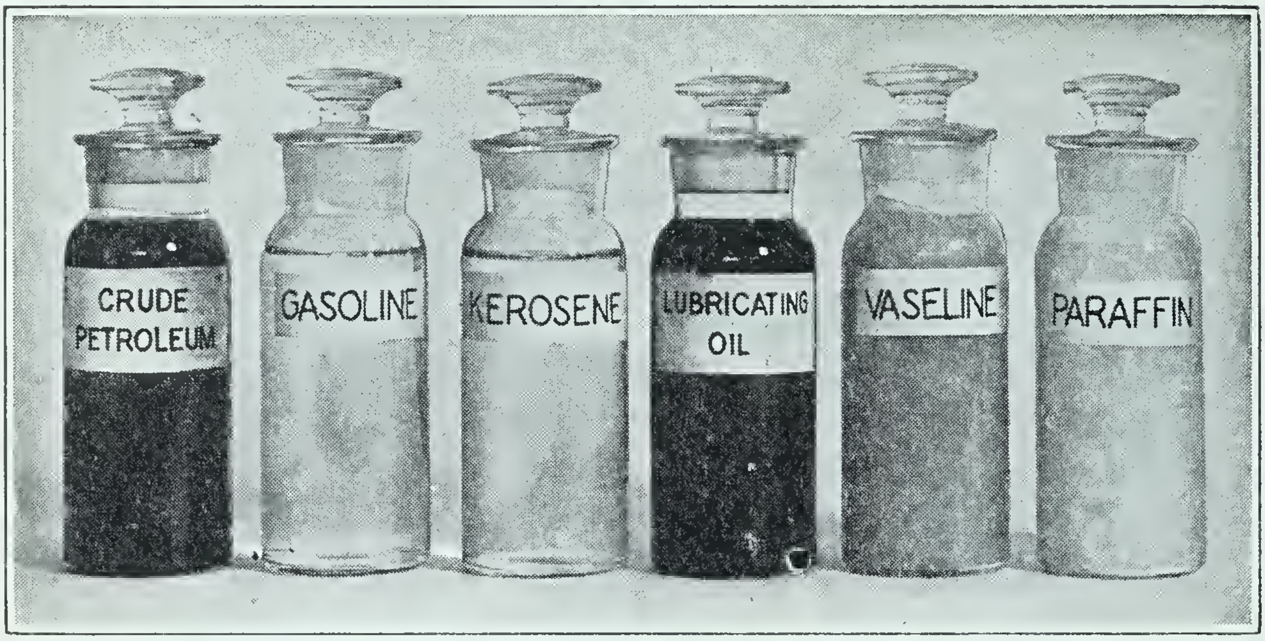

CRUDE PETROLEUM
GASOLINE
KEROSENE
LUBRICATING OIL
VASELINE
PARAFFIN

FIG. 313. Crude petroleum and some important products obtained from it

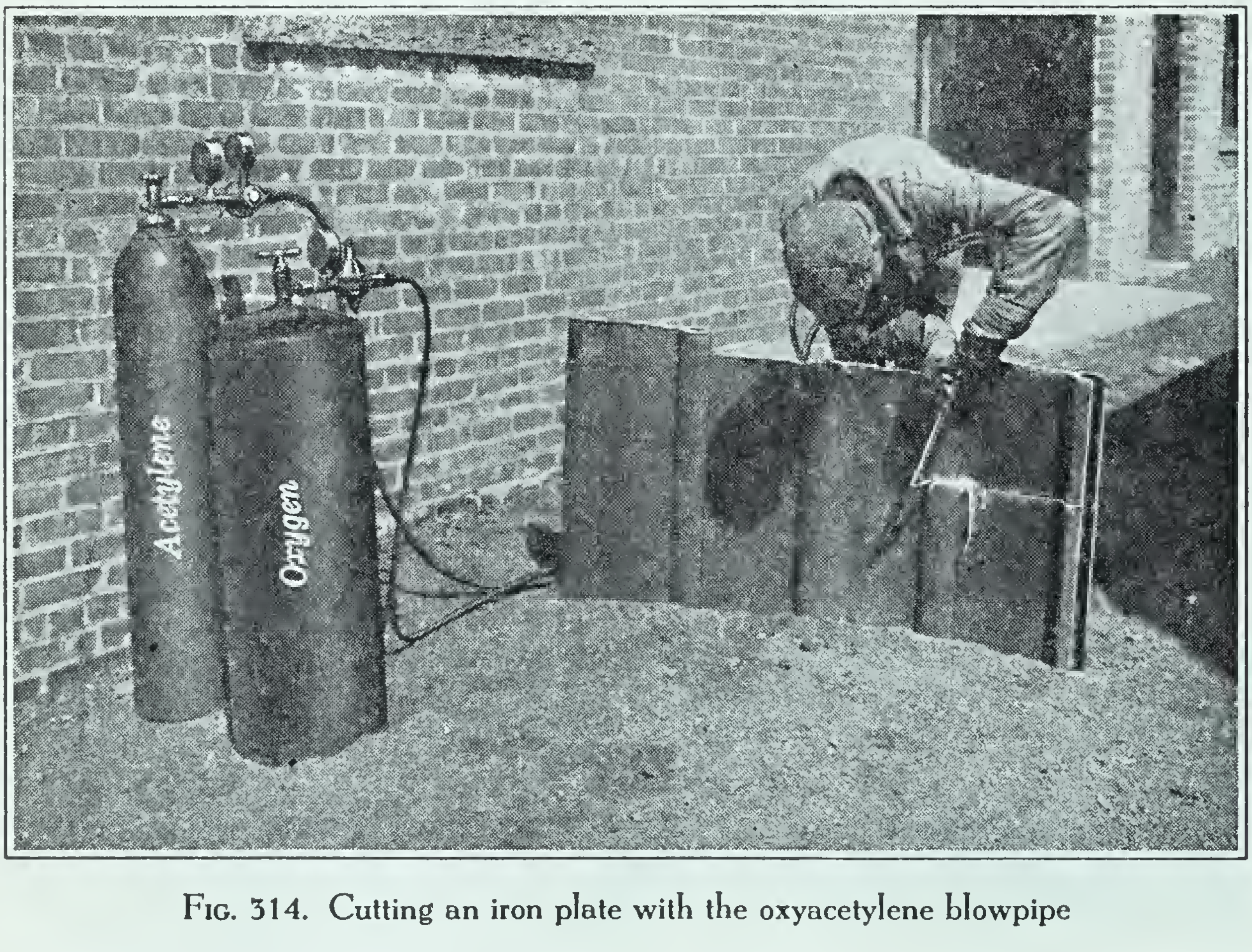

Acetylene
Oxygen

FIG. 314. Cutting an iron plate with the oxyacetylene blowpipe

To do this, the tip of the flame is held in contact with one spot of the metal until it is heated to a high temperature. Additional oxygen is then turned on, and the hot metal at once begins to burn away. If the tip of the flame is now moved slowly along the metal plate, the latter is cut apart

Methane (marsh gas) (CH_4). Everyone knows that various kinds of dead vegetable materials gather on the bottom of marshes or stagnant pools. Not so many have noticed that bubbles of gas rise to the surface of the water when the muddy bottom of a marsh is stirred. This gas is *methane*, often called marsh gas, and it is formed by the decay of the plant material in the absence of air.

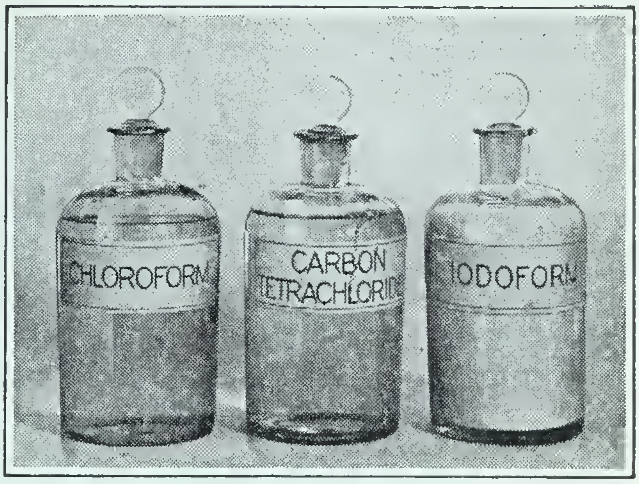


FIG. 315. Important halogen derivatives of methane

Pure methane is colorless, odorless, and about half as heavy as air. It is present in coal gas, and is the chief constituent of the natural gas which now has such a wide use as a fuel. Methane sometimes collects in coal mines, and when mixed with the air of the mines is called *firedamp*. (*Damp* is an old word for a gas or vapor.) Such mixtures are very explosive, and are the cause of some mine explosions (p. 448). When burned from a jet, the pure gas gives a pale-blue flame. The flame is very hot, giving 210,800 calories for each gram-molecule of methane burned, as expressed in the following equation:

$$CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O + 210{,}800\ \text{cal}$$

Halogen derivatives of methane. As a rule, the hydrogen of a hydrocarbon may be replaced by a halogen element, atom for atom. In this way a number of derivatives are formed from methane, the most important of which are the following (Fig. 315):

Chloroform, ($CHCl_3$), a heavy colorless liquid boiling at 61°, is the well-known anesthetic used in surgery. *Carbon tetrachloride* (CCl_4) boils at 78° and looks like chloroform. It is used in dry cleaning to remove grease spots from fabrics and has the advantage over benzine of being noninflammable. Large quantities are used as a fire extinguisher (Fig. 111). *Iodoform* (CHI_3) is a yellow crystalline solid and is often used as an antiseptic in dressing wounds.

Ethylene (C_2H_4). In addition to the hydrocarbons composing the methane series, many others are known. Ethylene is one of these. It is a colorless gas and burns readily with a hot flame. Coal gas contains a small percentage of it. In the laboratory it is made by taking away the elements of water from ordinary alcohol (C_2H_6O), as shown in the following equation:

$$C_2H_6O \longrightarrow C_2H_4 + H_2O$$

Ethylene has a number of uses, the most important being (1) as a source of heat, (2) as an anesthetic in surgical operations, and (3) as an agent for developing the natural color of citrus fruits, such as oranges and grapefruit. These fruits are often picked when green in color. This color changes to a yellow when the fruit is exposed to air containing a small percentage of ethylene.

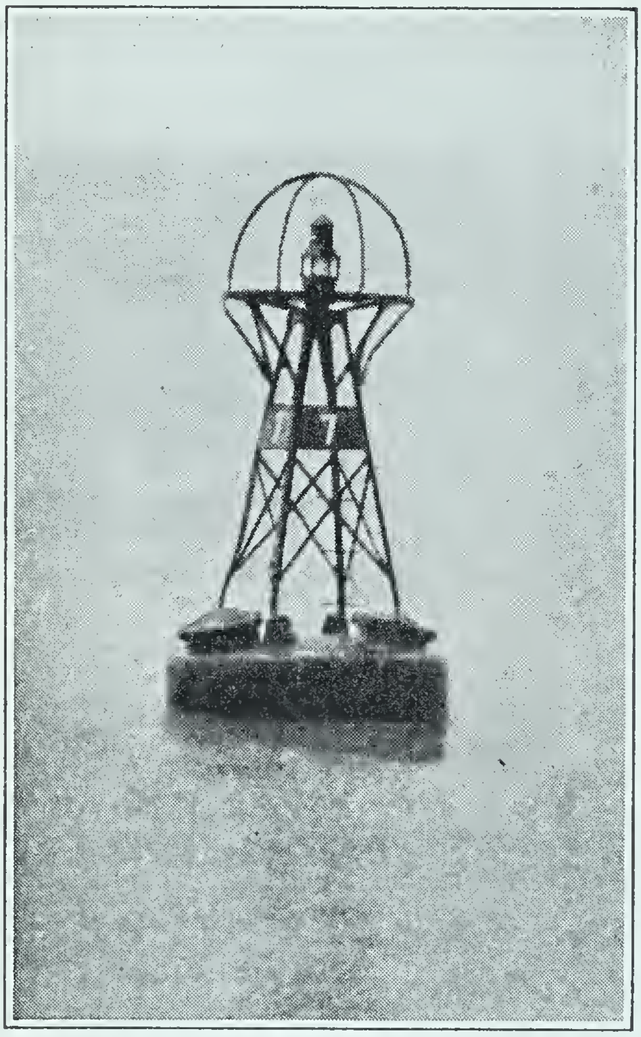


FIG. 316. Buoy lighted with acetylene, for marking ships' channels

Acetylene (C_2H_2). This hydrocarbon is a colorless gas easily obtained in the following way: When ordinary lime (CaO) is heated with carbon in an electric furnace, a solid compound called *calcium carbide* (CaC_2) is formed. When water is added to calcium carbide, the two compounds react to form acetylene, as shown in the equation

$$CaC_2 + 2\ H_2O \longrightarrow C_2H_2 \uparrow + Ca(OH)_2$$

In this way the gas is prepared in large quantities. When heated it decomposes, with evolution of a great deal of heat:

$$C_2H_2 \longrightarrow 2\ C + H_2 + 53{,}880\ \text{cal}$$

When compressed in steel containers, acetylene is very explosive, because the heat set free in compressing the gas is

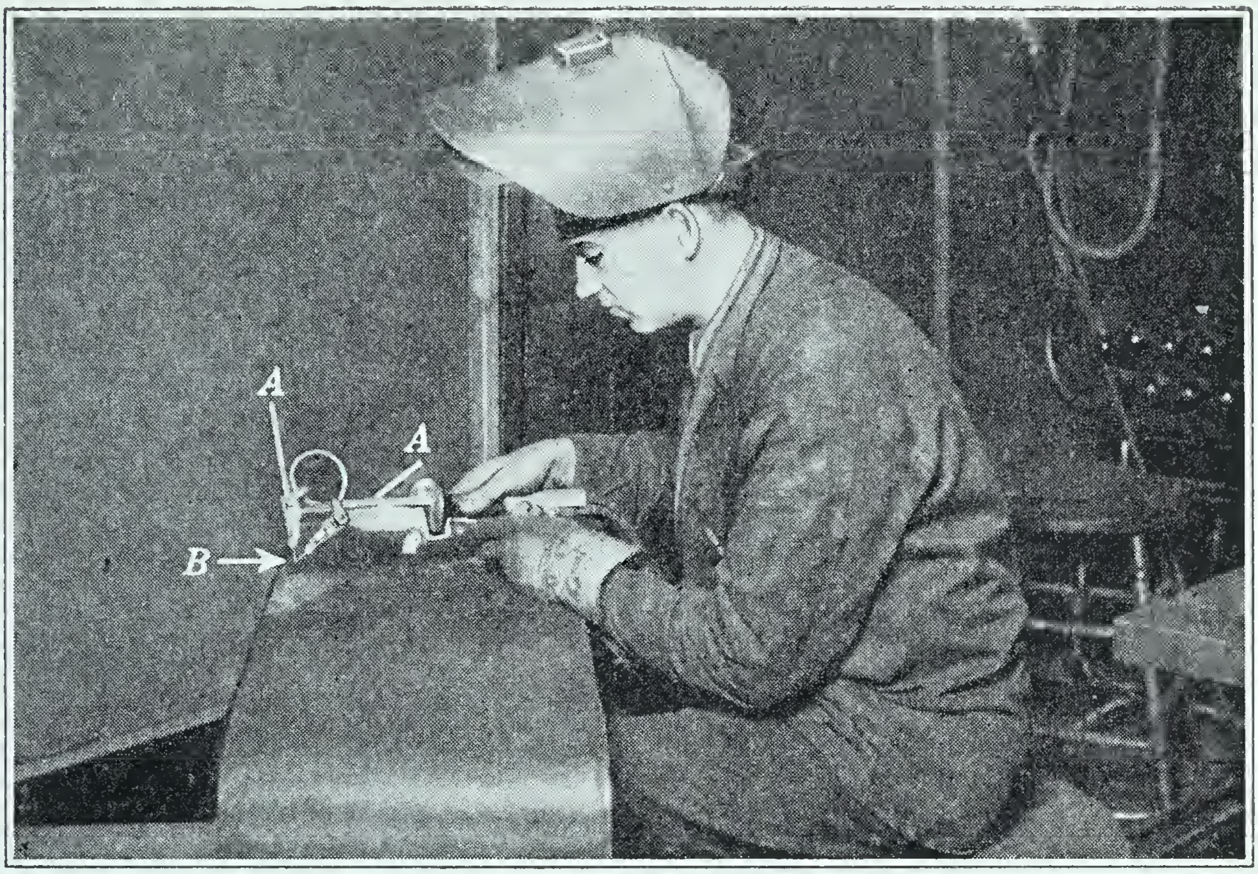


Fig. 317. The hydrogen-arc welding torch

An arc is formed at *B*, at the ends of the tungsten electrodes *A*, *A*. Hydrogen is fed into this arc, is parted into atoms, and then burns in oxygen

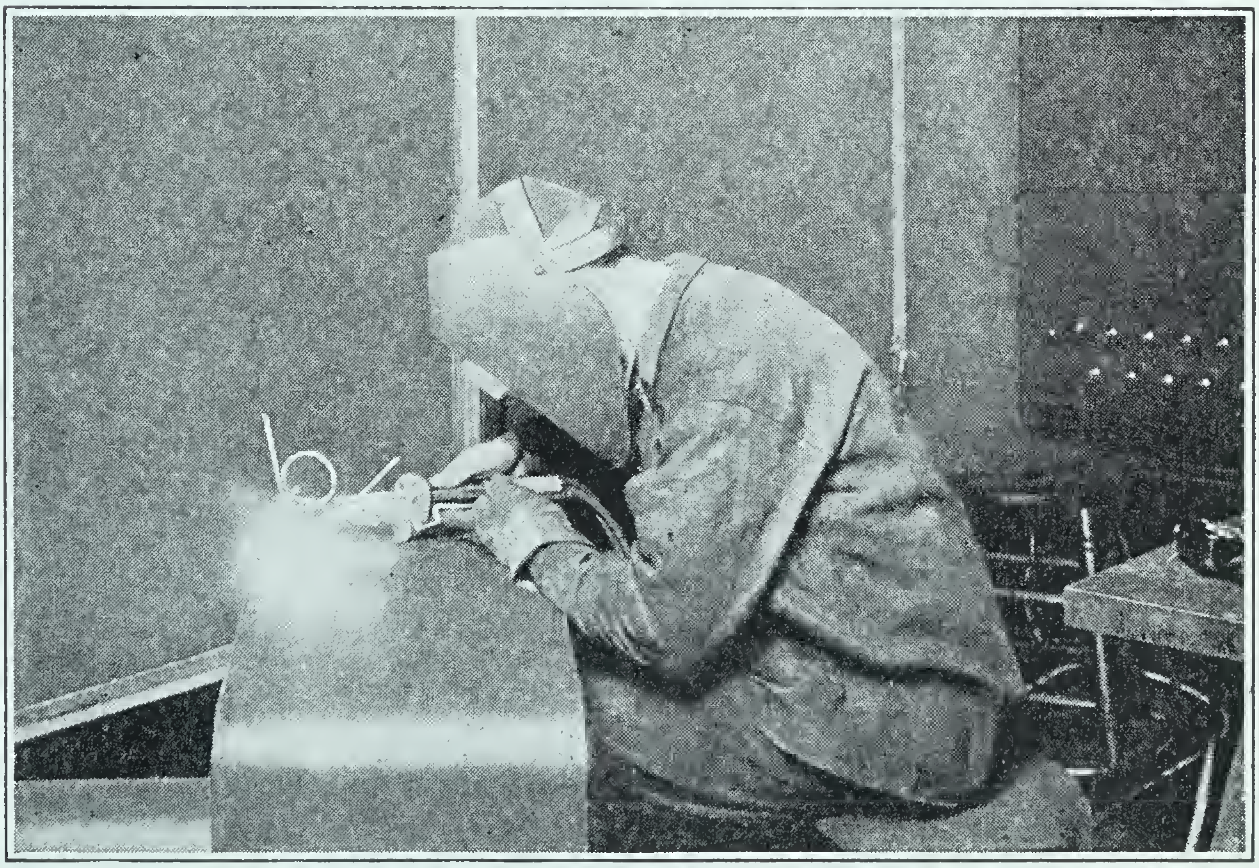


Fig. 318. The hydrogen-arc welding torch in operation

The operator protects his face and eyes by a hood and applies the flame of burning hydrogen to the object to be welded enough to start decomposition. It may, however, be stored safely in such containers if they are first filled with some porous material saturated with a liquid called acetone. Under pressure a large volume of the gas dissolves in the acetone. In this form acetylene is a common article of commerce.

The uses of acetylene. Formerly acetylene was widely used for lighting houses and hotels, but the electric light has now taken its place almost entirely. It is still used for lighting the buoys that mark ship channels (Fig. 316). Its chief use at present is in the cutting and welding of metals.

For these purposes acetylene is burned in pure oxygen in a device called the *oxyacetylene blowpipe.* This is like an oxyhydrogen blowpipe (Fig. 77), the only difference being that acetylene is used in place of hydrogen. By its use it is possible to weld metals and to cut into pieces old iron structures (Fig. 314).

Atomic hydrogen flames. In addition to the use of the oxyacetylene blowpipe, another method has been developed by the American chemist Langmuir (Fig. 116) for getting the high temperatures necessary for the welding of metals.

Langmuir found that when a current of hydrogen is passed through an electric arc between electrodes made of tungsten (the metal used in our electric-light filaments), the heat of the arc is sufficient to decompose the hydrogen molecules into atoms. As these atoms leave the electrode they immediately recombine to form molecules, setting free a large amount of heat in the process. This heat, together with the heat of combustion of the hydrogen, is much more intense than that of the oxyacetylene blowpipe. The apparatus for producing the flame is called the *hydrogen-arc welding torch* (Figs. 317 and 318).

CHAPTER SUMMARY IN QUESTION FORM

1. Give the following information in regard to those compounds composed of carbon and hydrogen only: (*a*) name; (*b*) number; (*c*) how classified; (*d*) name of most important series.

2. What relation exists between the boiling points of the members of the series referred to in question 1 and the number of carbon atoms present?

3. Give the names and formulas of the two products of complete combustion of each member of the series.

4. Which of the following statements is correct? Petroleum is composed of (*a*) a single liquid compound; (*b*) a mixture of liquid compounds; (*c*) a mixture of liquid compounds in which are dissolved both gaseous and solid compounds.

5. What name is given to the process of separating petroleum into several parts by distilling it and collecting the fractions that boil between certain limits of temperature?

6. Give the order in which the following products distill over in the process of refining petroleum: (*a*) fuel oil; (*b*) vaseline; (*c*) gasoline; (*d*) paraffin; (*e*) kerosene; (*f*) lubricating oils.

7. Name three compounds used in the purification of the above products.

8. Name (*a*) the most valuable petroleum product; (*b*) the process by which the amount obtained is greatly increased.

9. Petroleum is the principal source of gasoline. What other sources have we for it?

10. (*a*) What is the common name of methane? (*b*) How is it formed in nature? (*c*) What two useful gases contain it? (*d*) What name is given to a mixture of methane and air in mines? (*e*) Write the equation for the complete combustion of methane.

11. (*a*) Write the equation for the reaction of water with calcium carbide. (*b*) What is the name of the hydrocarbon formed?

12. What name is given to the process of heating two pieces of metal to their melting points and so causing them to fuse together?

13. Give the name of (*a*) a compound and (*b*) the instrument used for producing the heat necessary for the process referred to in question 12.

14. (*a*) Substitute the word *element* for the word *compound*, in question 13, and then answer the question. (*b*) Why is the heat produced in this case so very intense?

THOUGHT QUESTIONS

1. Name the properties of gasoline that (*a*) make it useful in our homes; (*b*) make it dangerous.

2. Explain why hydrogen, oxygen, chlorine, carbon dioxide, and many other gases can be compressed in empty steel cylinders with safety, while acetylene cannot.

3. Write the equations for the reactions that take place when each of the following gases burn: (*a*) methane; (*b*) ethane; (*c*) propane.

4. How do you account for the carbon monoxide in the exhaust of a gasoline engine?

5. Write the equation for the complete combustion of acetylene. By looking at the equation, tell (*a*) in what proportions, by volume, acetylene and oxygen will combine; (*b*) also the proportion of each of these to the volume of the carbon dioxide formed.

6. A certain stove burns 300 cu ft of natural gas daily. Assuming that the gas is pure methane, (*a*) what volume of oxygen is required for the complete combustion of the gas? (*b*) what volume of carbon dioxide is formed? (Use Avogadro's law, pp. 213–214.)

7. A given volume of hydrogen burns in the air with a very hot flame. How can the intensity of the heat be increased without increasing the pressure?

8. Some petroleum contains sulfur compounds. Give reasons why these must be removed.

9. Should you expect a solid to be left after the evaporation of (*a*) gasoline? (*b*) kerosene? (*c*) petroleum?

OPTIONAL EXERCISES

1. Write a theme on the subject "The Uses of Petroleum and of the Products Obtained from It."

2. Collect a set of samples of petroleum products for your school.

CHAPTER XXXVIII

Fuels—They Give Us Heat and Power

The first fuels used. Wood was the first fuel to be used, not only because it was always at hand but also because the cleared ground was needed for growing food. Next came charcoal, made from wood; and this was useful not only as a fuel but also as a reducing agent in getting the metals from their ores. Then it was found that certain black stones (coal) would burn, making a hot fire.

But the smoke from these "stones" raised protests on the part of many persons living in the large cities, and as late as the thirteenth century the use of coal was forbidden in London. Later, Queen Elizabeth stopped its use as a fuel during sessions of Parliament because "the health of the knights might suffer during their abode in the metropolis." As wood became scarcer the great advantage of coal overcame all objections to its use, and it is only in recent years that attention has again been called to the smoke nuisance.

The latest fuels to come into use are (1) petroleum and the fuel oils obtained from it, and (2) the various fuel gases.

The elements present in fuels. All fuels contain carbon, and most of them hydrogen as well. In addition, some of them have other elements (especially oxygen in wood), but it is the carbon and hydrogen that give them their fuel value. When the fuels burn, the hydrogen and carbon unite with the oxygen of the air to form water and carbon dioxide (or carbon monoxide, if the oxygen supply is limited).

GASEOUS FUELS

The different kinds. Gaseous fuels have many evident advantages that need not be explained. In most places they cost more than other kinds of fuel, but the advantages often outweigh the extra cost. The most important of these fuel gases are (1) coal gas, (2) water gas, (3) producer gas, and (4) natural gas. Each of these will now be described in turn.

Coal gas. It has been known for several centuries that when soft (bituminous) coal is heated out of contact with air, combustible gases are formed. Indeed, gas prepared in this way was used for street-lighting in London, Paris, and Baltimore more than one hundred and twenty-five years ago.

When coal is heated in closed vessels or retorts which shut out all the air, very complex changes take place. Various gaseous compounds which constitute coal gas are formed, as well as ammonia (p. 289) and a thick, black mass called coal tar. All these products are vaporized by the heat and led away through pipes, leaving the nonvolatile coke in the retort. *In the manufacture of coal gas, then, we get not only coal gas, coke, and ammonia, but also coal tar, which is the source of hundreds of useful compounds.* The more important steps in the process are given in Fig. 319.

By-product coke ovens. The coke obtained in the manufacture of coal gas is a very important thing, useful not only as a fuel but especially as a reducing agent in getting such metals as iron from their ores. The quantity of coke obtained in the manufacture of coal gas has never been large enough to meet the demand. Much of the additional coke required has been made by heating the coal in *beehive ovens*, so named because of their shape. This is a very wasteful method, because all the by-products (coal gas, ammonia, and coal tar) escape into the air and are burned. This process has now given way almost entirely to one in which coal is heated in a *by-product coke oven* (Fig. 320), which makes it possible to save all the products formed.

Water gas. Water gas is practically a mixture of carbon monoxide and hydrogen. It is made by passing steam over hot anthracite coal or coke, when the reaction shown in the following equation takes place:

$$C + H_2O \longrightarrow CO\uparrow + H_2\uparrow$$

The coal is burned in a draft of air until it is very hot. The air is then shut off and the steam turned on. The temperature gradually falls, because the reaction absorbs heat. When it reaches about 1000°, the steam is cut off, the air supply renewed, and the process repeated.

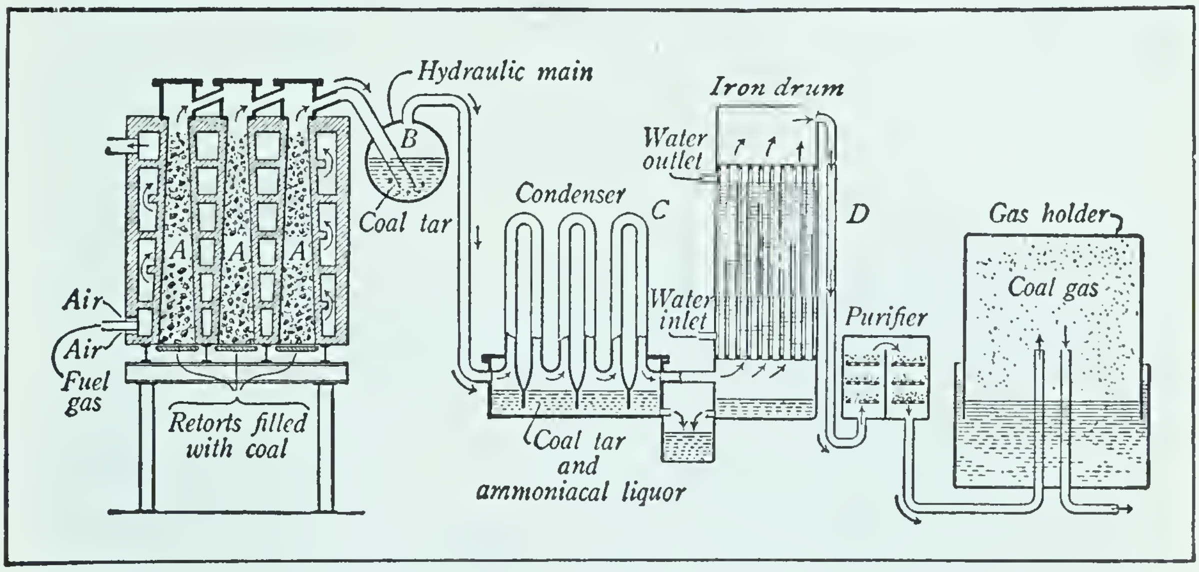


FIG. 319. Diagram showing the essential parts of the apparatus used in the manufacture of coal gas

The coal is introduced into rows of closed retorts, *A*, *A*, *A*, and heated. A delivery pipe leads from the top of each of the retorts into a large pipe *B* (known as the *hydraulic main*). The application of heat causes the coal to undergo complex changes which result in the formation of a large number of compounds. These compounds escape through the delivery pipe into the hydraulic main. The temperature being reduced, some of the products that are solid or liquid at ordinary temperatures condense in the hydraulic main in the form of a dark liquid known as *coal tar*. The gases then pass on into the condenser *C*, in which the products are cooled to such an extent that the remaining tar is deposited. Along with the tar is condensed a liquid (chiefly water) containing ammonia in solution and known as *ammoniacal liquor*. The gas is then led into a large iron drum *D*, fitted with copper tubes, through which the gas passes. The tubes are kept cool by running water, and further condensation of vapors takes place in the tubes. From the drum *D* the gas passes into the purifier, where it comes into contact with lime or iron oxide, which removes any sulfur compounds present; from this it enters the large gas holder, from which it is distributed to consumers. The great bulk of the carbon remains in the retort as *coke* and as *retort carbon*. The yield of gas, tar, and soluble materials depends upon many factors, such as the composition of the coal, the temperature employed, and the rate of heating. One ton of good gas coal yields approximately 10,000 cu ft of gas, 1400 lb of coke, 120 lb of tar, and 20 gal of ammoniacal liquor

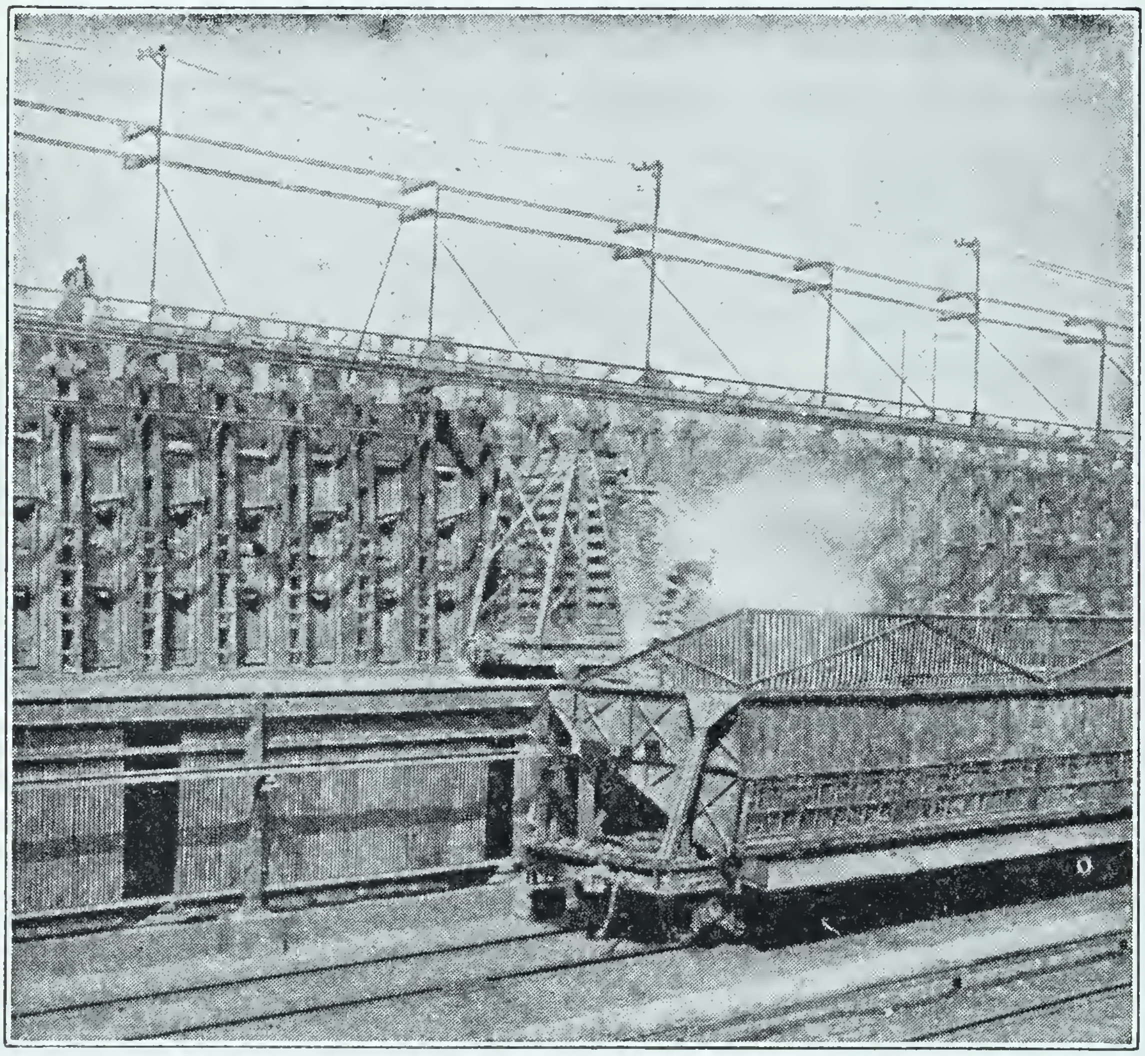


Fig. 320. View of a portion of a large by-product coking plant

The plant consists primarily of a number of narrow upright ovens placed side by side but separated by combustion chambers so as to admit of heating the coal with which the ovens are filled. Sometimes a portion of the gas generated in the process is used as a fuel for coking the coal; more often this is saved and the much cheaper *producer gas* (p. 441) used in its place. The hot flame of the burning gas strikes against the bottom and sides of the ovens. The coal tar and the ammonia are separated and collected as in the manufacture of coal gas; indeed, the by-product oven is a large coal-gas plant. When the process is complete, each oven is pushed forward and the coke dropped into a car, as shown in the figure. The by-product ovens are rapidly displacing the older beehive type. Of the nearly 50,000,000 tons of coke produced annually in the United States, more than three fourths is produced in the by-product ovens. Over 80 per cent of the output of coke is used in reducing iron from its ores

Water gas is a good fuel, since both carbon monoxide and hydrogen burn with a very hot flame. It is usually *enriched* by mixing with it petroleum vapors.

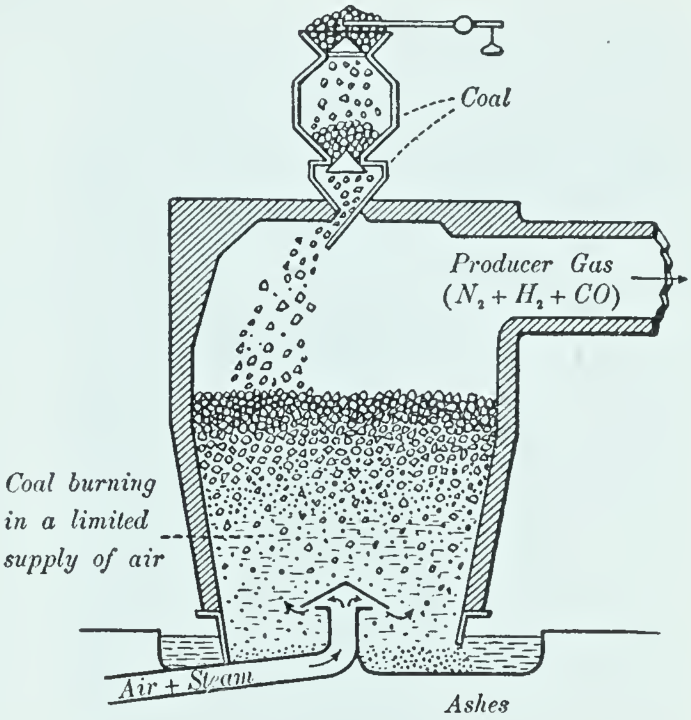


FIG. 321. Diagram illustrating the manufacture of producer gas

Producer gas. This fuel is especially useful in reducing the metals from their ores. It is also used as a fuel for gas engines. It is made by burning coal in a very limited supply of air so that the product of combustion is largely carbon monoxide (Fig. 321). At the same time, steam is admitted with the air, and this, upon passing through the hot bed of coals, is reduced as in the manufacture of water gas. Made in this way, producer gas is mainly a mixture of carbon monoxide, hydrogen, and nitrogen. It can be made from coal of a poor quality and is the cheapest way to use low-grade coal for power. Since more than half of the gas is nitrogen (see composition of producer gas in table below), it has a low heat of combustion. This disadvantage is offset by the low cost of making the gas.

AVERAGE COMPOSITION OF DIFFERENT FUEL GASES, EXPRESSED IN PERCENTAGE BY VOLUMES

CONSTITUENT	OHIO NATURAL GAS	COAL GAS	WATER GAS	PRODUCER GAS
H_2	—	52.0	47.5	12.0
CH_4	80.0	32.0	1.0	3.5
C_2H_6	17.7	—	—	—
CO	—	6.0	43.5	25.5
CO_2	—	2.0	3.5	5.0
N_2	2.0	3.0	4.5	53.5
O_2	—	0.3	—	—
Other hydrocarbons .	0.3	4.7	—	.5
Heat values in calories per cubic meter . .	10,000	5350	2690	1370

Natural gas — the ideal fuel. This is found stored under great pressure in the earth, nearly always along with petroleum; and, like petroleum, it is got by drilling wells into the gas-bearing rock strata (Fig. 322). While natural gas from different places varies in composition, it is nearly always made up chiefly of methane mixed with small percentages of other hydrocarbons. The methane content of natural gas averages approximately 80 per cent. A small percentage of nitrogen is often present, and the gas from a few wells is over one-third nitrogen. Natural gas with such a high percentage of nitrogen usually contains helium; and, in fact, this is the commercial source of helium (p. 271).

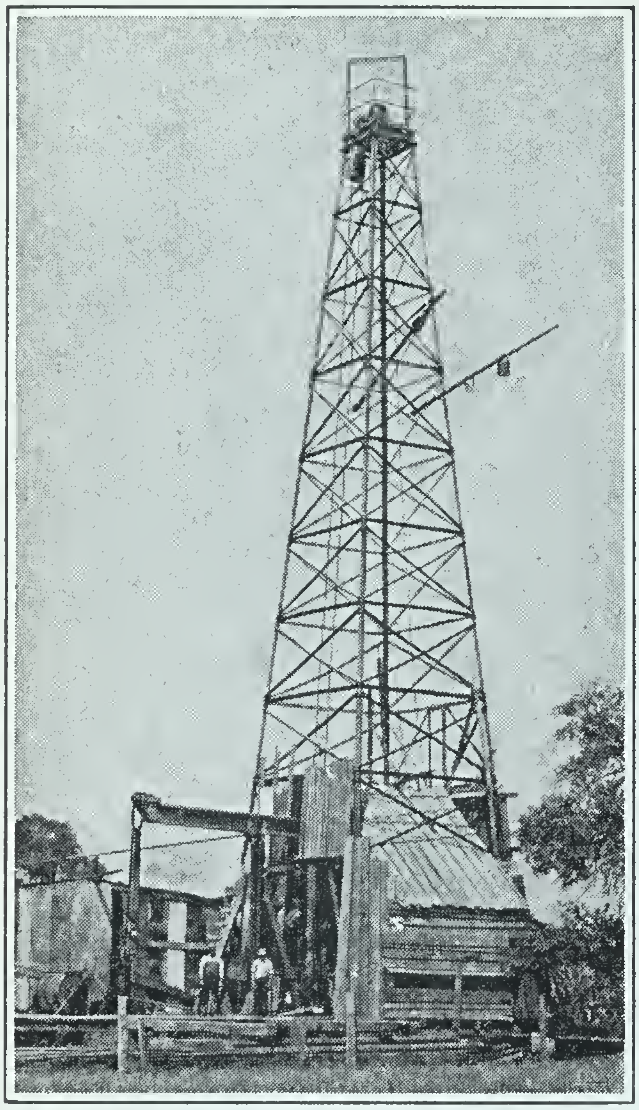


Fig. 322. Drilling a well for natural gas in a West Virginia field

Natural gas burns with a hotter flame than do any of the other fuel gases and is an ideal fuel. A given volume of it, when burned, will give off almost twice as much heat as will an equal volume of coal gas, and more than seven times that given off by producer gas.

Comparative composition of fuel gases. In the table on page 441 are given the average analyses of many samples of each of the different fuel gases. Since the composition of different samples of the same kind of gas varies considerably, the values are approximate only.

It is difficult to exaggerate the value of these fuel gases. They give a great deal of heat just when and where we want it; they burn with a clean flame, a fact of great importance in industry; they leave no ashes and thus lighten work.

SOLID AND LIQUID FUELS

The use of coal, coke, and charcoal as fuels has been described in Chapter XI. Petroleum and certain oils have come into wide use in recent years, not only for heating our homes but especially as fuel for ships and railway engines. The oil is sprayed into the furnaces and the fireboxes by compressed air and is burned. In the Diesel engine, which is now coming into wide use, it is sprayed directly into the cylinders of the engine.

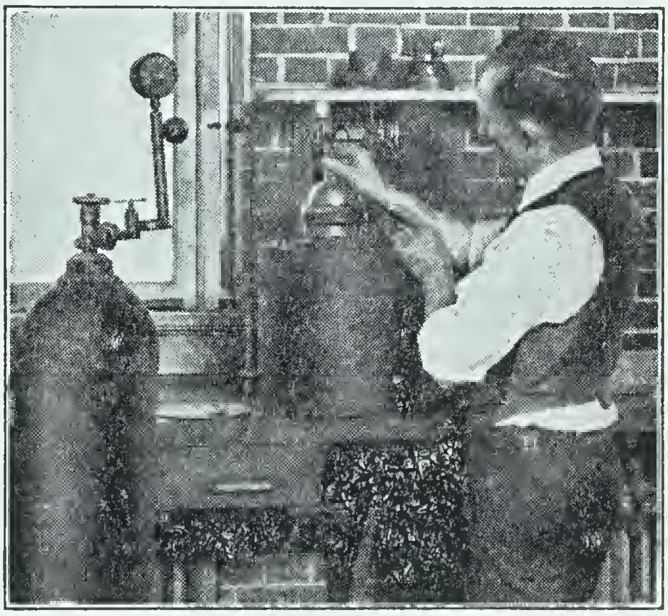


Fig. 323. Determining the calorific value of coal

Heat values of fuels. The various materials used as fuels differ much in the heat evolved when they are burned. While there are many other factors in the value of a fuel, the chief one is its *heat of combustion.* In describing a fuel gas it is customary to give the number of calories of heat evolved in the combustion of a definite volume of the gas, such as one cubic meter (see table, p. 441). With *solids* the heat value is expressed in terms of the *calorific value* of the fuel. This is *the heat evolved in the combustion of one gram of the fuel.* Sometimes the heat value is given in British thermal units (B.T.U.), this unit being the heat required to raise the temperature of 1 lb of water 1° Fahrenheit (1 B.T.U. = 252 cal).

In large contracts the price paid for a fuel is usually based on its calorific value as well as its fitness for the use to which it is to be put. The calorific value of a solid fuel — say, coal — is measured by burning a weighed sample in a bomb calorimeter, which consists of an airtight metal vessel filled with oxygen and surrounded by water (Fig. 323). The heat evolved is taken up by the water, and the increase in the temperature of the water is noted. The table on page 444 gives some average values for a few common solid fuels.

Calorific Value of Some Solid Fuels

Wood (air-dried)	about 3800–4000 cal
Bituminous coal (Pennsylvania), 35% volatile matter, 6% ash	about 8000 cal
Bituminous coal (Pocahontas), 18% volatile matter, 6% ash	about 8300 cal
Anthracite coal, 12% ash	about 7300 cal
Coke, 10% ash	about 7300 cal

Smoke prevention. The American chemist Weinlein recently said: "One of the biggest problems we are facing is the smoke nuisance. Smoke does not have a single saving grace. It is injurious to health. It is expensive in that it means fuel waste, high laundry bills, defacement of expensive buildings, and lessened working capacity. Experts declare that throughout the United States smoke costs each inhabitant $16 annually." So a very important question is, Can smoke be prevented, and, if so, how?

Since the main products of the combustion of fuels are carbon dioxide and water vapor, both of which are colorless gases, we see that if the combustion is complete there will be no smoke. Unfortunately, in the way coal is burned in most of our homes and factories the combustion is not complete, and large amounts of finely divided carbon and tarry matter are poured into the air. *We can prevent smoke by getting complete combustion of the fuel.* The necessary conditions for doing this are (1) an adequate supply of air; (2) thorough mixing of the air above the fire bed with the combustible gases coming from the fuel; (3) a temperature high enough to keep up active combustion. Many "smoke-consuming" furnaces are now made, which, it is claimed, are so designed as to bring about complete combustion.

FLAMES AND EXPLOSIVE MIXTURES

What causes a flame? When a burning substance stays solid at the temperature reached in combustion, light is given off, but there is no flame. Iron wire burning in oxygen throws off a shower of sparks, but no flame is seen. When, however, both of the substances taking part are gases or vapors *at the temperature reached in combustion*, the act of union is accompanied by a flame. Many solids (and liquids), such as a candle, burn with a flame; but this is because the heat of combustion first melts the solid and then vaporizes the liquid, the flame being the result of the union of this vapor with the oxygen of the air. That the interior of a candle flame is made up of combustible vapor can be proved by holding one end of a glass tube in the flame, as is shown in Fig. 324. Some of the vapor escapes through the tube and may be lighted at the upper end of the tube.

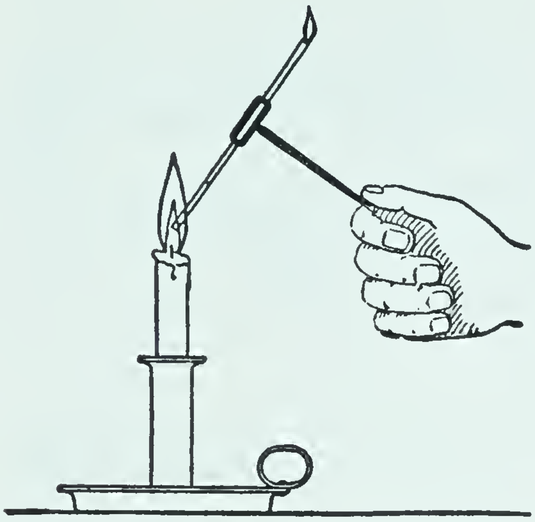


Fig. 324. The interior of a candle flame contains combustible vapors

Structure of a flame. When carbon monoxide or hydrogen burns in oxygen, only one reaction takes place, and as a result the flame is very simple in structure. It consists of a colorless inner cone of unburned gas, and an outer cone in which the union between the gas and the oxygen is taking place. That the inner cone is cool may be shown by suspending a match head in this region and lighting the gas. The match is not set on fire by the flame surrounding it.

The flames produced by the combustion of hydrocarbons such as are present in coal gas and natural gas, or of mixtures of hydrocarbons with related compounds as in candles, are much more complex because several reactions take place one after the other. For example, in the candle flame (Fig. 325) there are, broadly speaking, three cones: (1) The inner cone *A*, composed of combustible vapors. (2) A middle cone *B*, in which these vapors are decomposed by the heat. A small quantity of carbon is also set free, which, being heated to incandescence, makes the flame luminous. (3) An almost

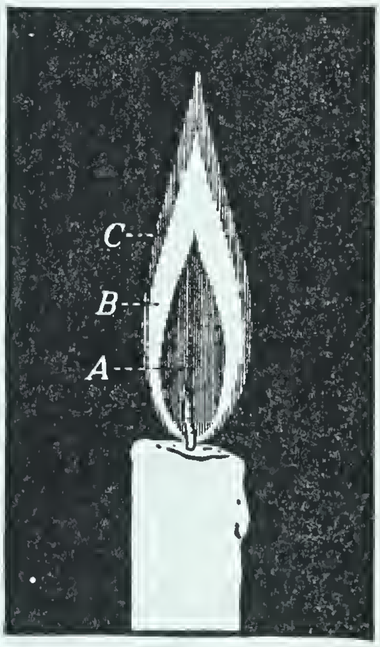


Fig. 325. The cones of a candle flame

invisible narrow outer cone, or film, *C*, in which the hydrogen and carbon are burned to water and to carbon dioxide.

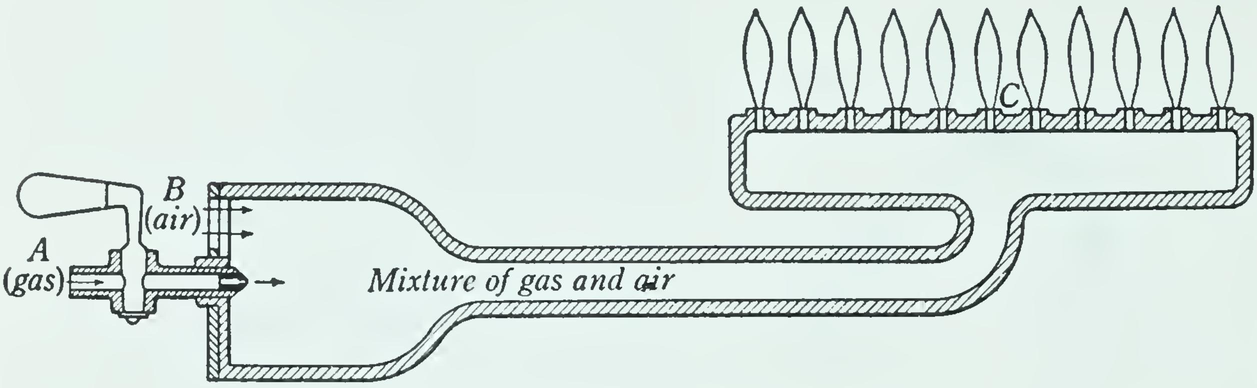


FIG. 326. Cross section of a common gas burner

Gas is admitted at *A*, and ignited at *C*. Sufficient air is drawn in through *B* to make the flame colorless or nearly so

Some common gas-burners. The common fuel gases, such as natural gas and coal gas, flowing from a small pipe, burn with a luminous flame. Such a flame is not very useful, because it deposits carbon on the burners or on the objects heated. The combustion can be made complete and the flame made nonluminous or nearly so by mixing the gas with a certain percentage of air a short distance before it reaches the end of the pipe. This is done by having an opening (mixer) in the base of the burner, into which the air is drawn by the flow of the gas. The burners are fitted with some simple device, such as the band on the Bunsen burner, so that by proper adjustment precisely the right amount of air may be admitted (Figs. 326, 327) to ensure complete burning.

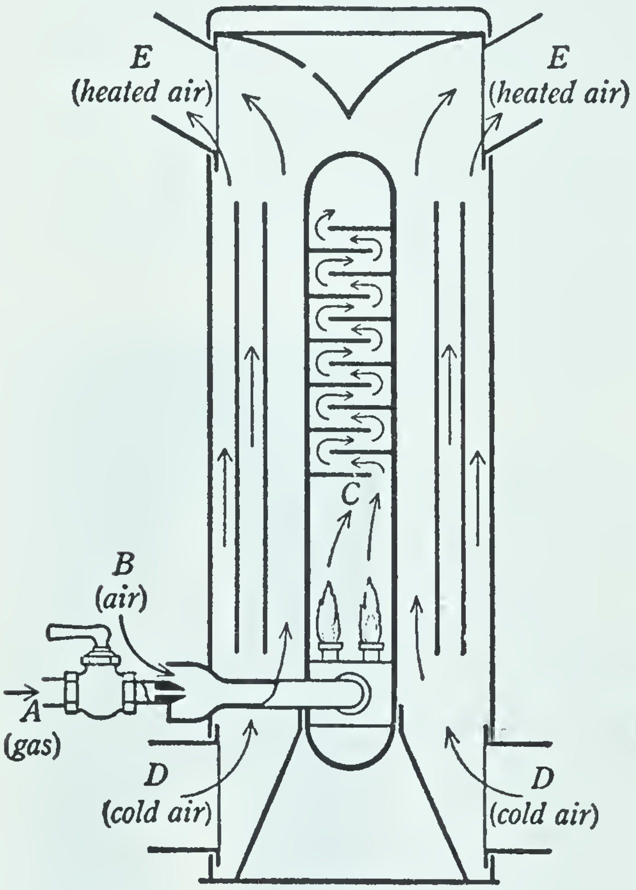


FIG. 327. A vertical cross section of a simple gas furnace

The gas is admitted at *A*, and sufficient air at *B* to make the flame colorless at *C*. The flame and hot products of combustion heat the metal partitions, and these heat the cold air entering at *D*, *D*. The heated air passes out through the pipes *E*, *E* to the different rooms of the building

Oxidizing and reducing flames. The tip of the flame of a candle or of a Bunsen burner is very hot and air is abundant, so that anything heated in this part of the flame tends to be oxidized. So we call this part of the flame the *oxidizing flame.* The tip of the luminous cone (*B*, Fig. 325), on the other hand, contains the highly heated reducing gases hydrogen and carbon monoxide, and this part of the flame is called the *reducing flame.* Many metallic oxides, such as lead oxide, when heated in the reducing flame, are very easily reduced to metals.

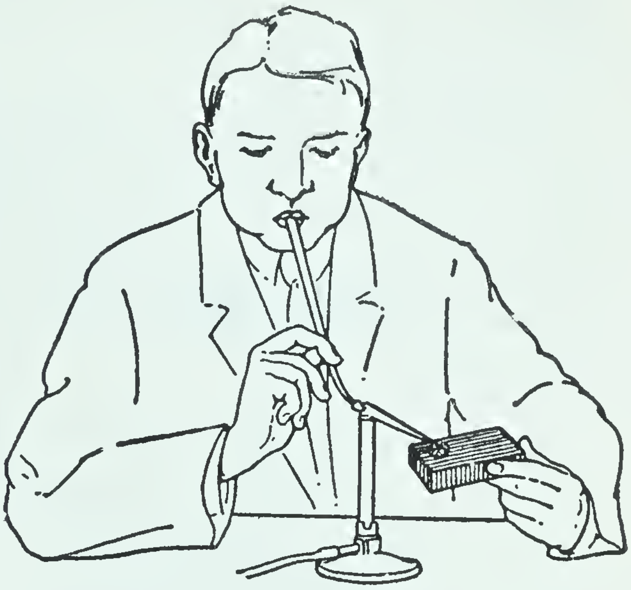


Fig. 328. Heating a metal in the oxidizing flame

Blowpipe tests. We can sometimes get information quickly as to what a substance is by trying the effect of the oxidizing and the reducing flame on it. This is easily done by using a mouth blowpipe, as shown in Fig. 328. The blowpipe is a metal tube bent at one end and drawn out to a fine opening. If the end of the tube is placed just at the edge of a small flame, and a current of air is blown through the tube, the flame is bent at an angle, as shown in the figure. The tip of the flame is the oxidizing flame; the interior is the reducing flame. The substance to be tested is placed in a cavity on a piece of charcoal and held so that the desired part of the flame strikes it.

Explosions. We often read of some disastrous explosion caused by the escape of fuel gas in a house. It is of interest to study the cause of explosions and to learn the reason for their terrific power.

An explosion is due to a sudden chemical reaction in which the volume of the gases formed in the reaction is much larger than that of the reacting substances.

So if the reacting substances are confined, as in a room or in a gun barrel, something must give way. The greater the change in volume in a rapid reaction, the more violent will be the explosion that results. Sometimes this increase in volume is due entirely to the heat evolved in the reaction (Charles's law, p. 43).

Explosive mixtures. But another question arises. Suppose we are cooking with a gas range. It is probable that every time we light the gas a little of it escapes into the room, but no explosion takes place. Just how much of the gas can be present in the air of the room before it forms an explosive mixture?

Experiments have shown that there is no danger of an explosion unless the mixture of air and gas falls between certain limits in percentage composition; also that these limits are perfectly definite for each kind of fuel gas under the same conditions. For natural gas (methane) the limits are about 5 and 14. That is, natural gas escaping into the air of a room will not form an explosive mixture until the gas reaches 5 per cent by volume of the mixture; and the mixture will cease to be explosive if the amount of gas exceeds 14 per cent. For coal gas the limits are about 6 and 29, and for acetylene the limits are 2.5 and 73.

Mine explosions. Most mine explosions are due to the presence of finely divided carbon in the air of the mine. A few are due to methane in sufficient percentages to form an explosive mixture (p. 433). Such mixtures will not explode unless the gases are heated to their kindling temperature *at some point* in the mixture. So a small flame or even a spark is enough to start the explosion. Formerly miners used an open-flame oil lamp, and this would set off any explosive mixture with terrible results.

The safety lamp. In 1815 the English chemist Sir Humphry Davy (Fig. 163) invented a miner's lamp in which the usual chimney of a lantern is replaced by wire gauze (Fig. 329). A flame starting at the wick is so cooled by the wire gauze that burning stops, and the flame is confined inside the wire chimney of the lamp (Fig. 331). The principle may be demonstrated by holding a sheet of wire gauze horizontally several inches above a Bunsen burner (Fig. 330). If the gas is turned on and lighted above the gauze, the flame

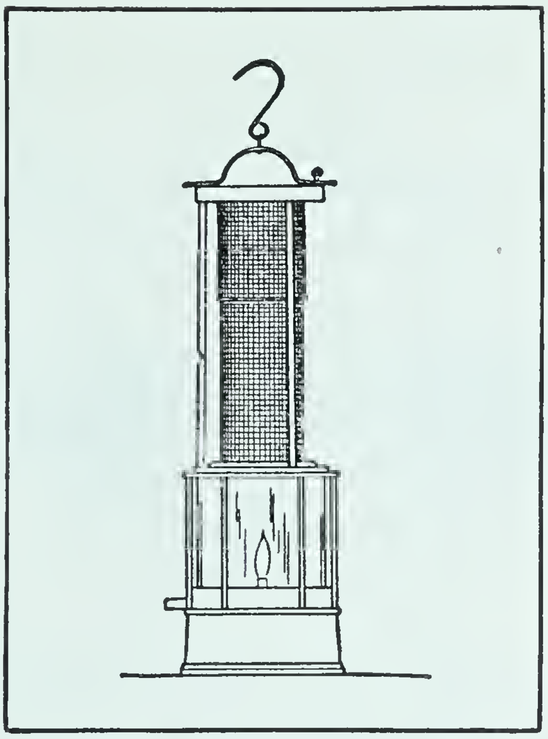


Fig. 329. The miner's safety lamp invented by Davy

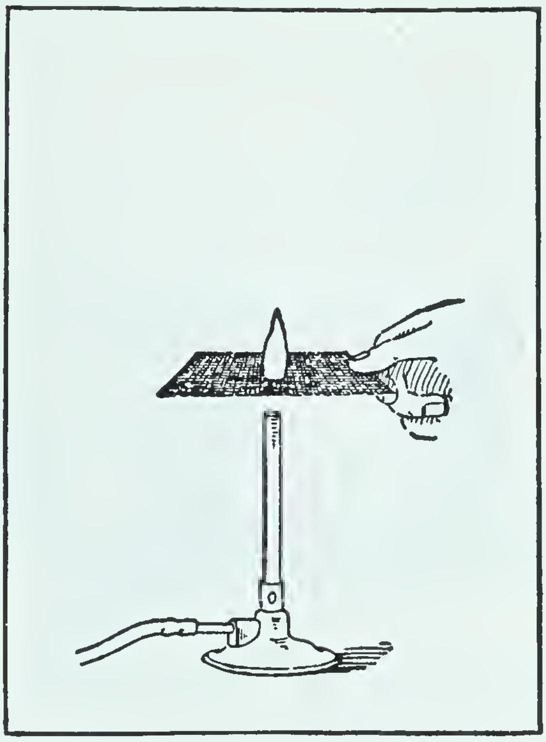


Fig. 330. Experiment illustrating the principle of the safety lamp

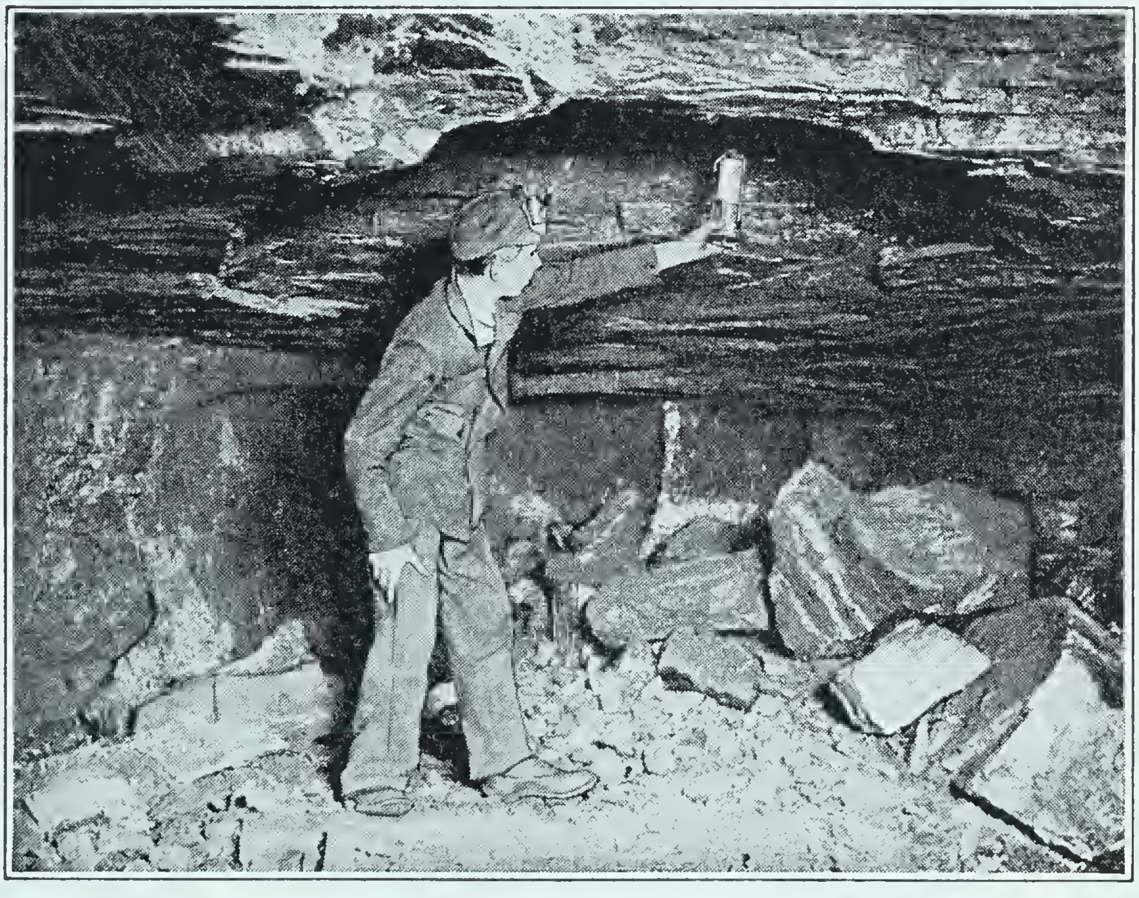


Fig. 331. Testing for pockets of explosive gas mixture in a mine

A series of small explosions within the safety lamp gives warning of the presence of a dangerous explosive mixture

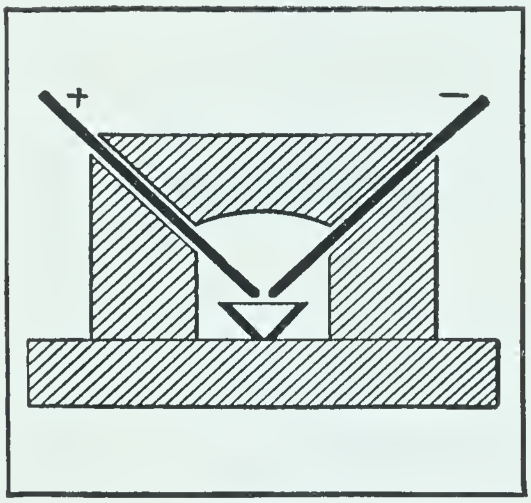


Fig. 332. An electric-arc furnace

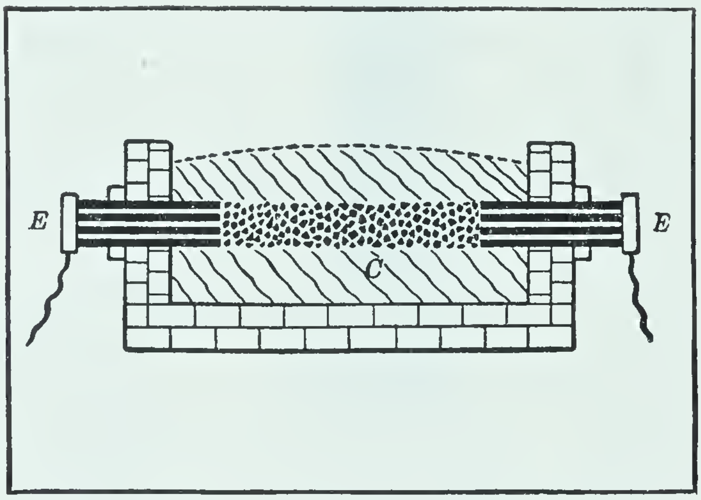


Fig. 333. An electric-resistance furnace

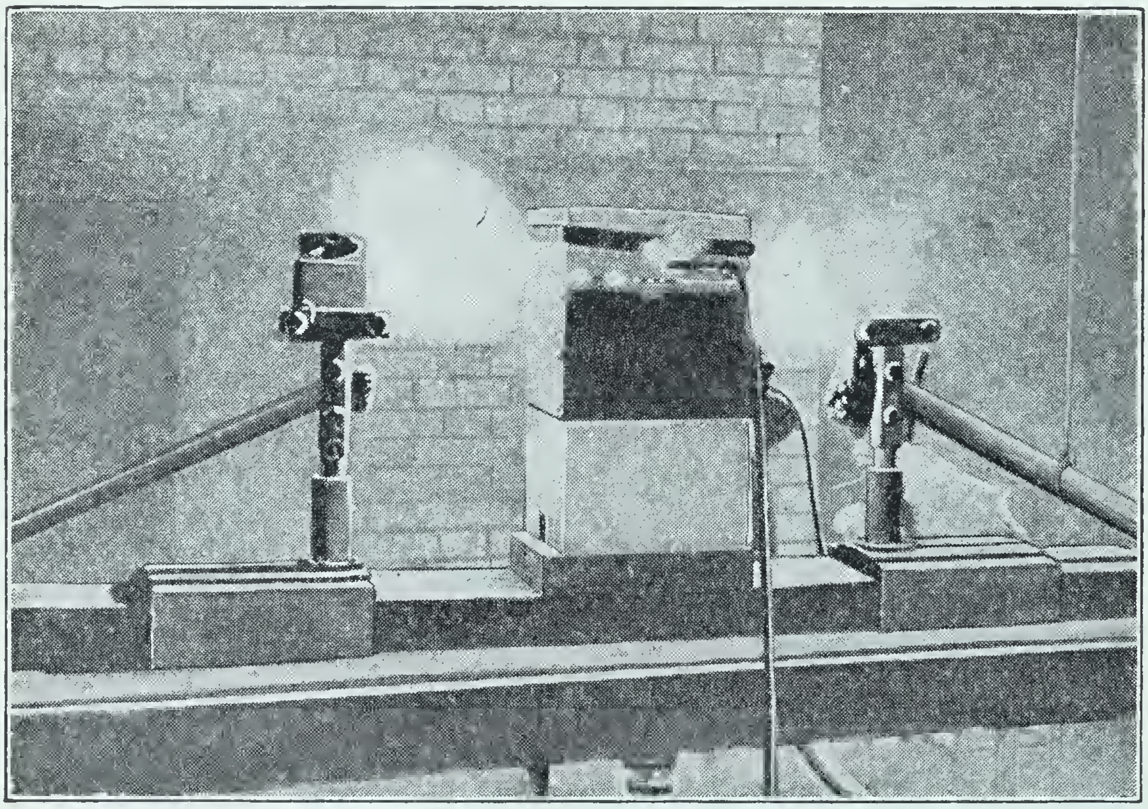


Fig. 334. View of an electric furnace used by Moissan, one of the first scientists to experiment with reactions at high temperatures produced in electric furnaces

From Duncan's *Chemistry of Commerce*

rests upon the gauze but does not go below it. At present small electric lamps, operated by pocket storage batteries, are frequently used by miners in place of gas lamps.

What makes our automobiles go? We are apt to think of explosions as being dangerous things, tearing down buildings and killing people; and so they often are. Yet when properly controlled they may be made to do us a very good turn. For example, it is the explosion of a mixture of gasoline vapor and air in the cylinders of the gas engine that runs our automobiles. The carburetor of the engine is simply a device for vaporizing the gasoline and mixing the vapor with the proper amount of air to form an explosive mixture. This mixture is then led into the cylinder of the engine and exploded, as explained in Fig. 335.

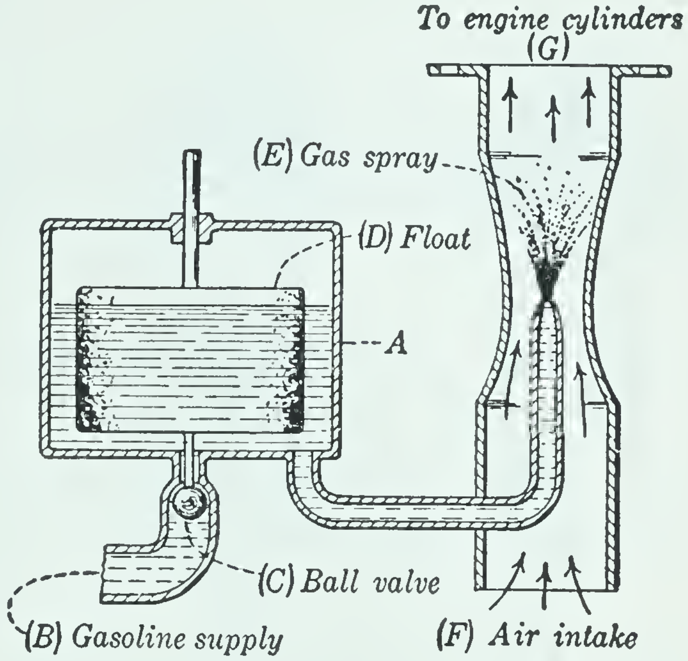


Fig. 335. Simplified diagram of a carburetor

Entering the carburetor at *B*, and kept at a constant level in *A* by the float *D* and ball valve *C*, the gasoline issues as a fine spray from the jet *E* and forms an explosive mixture with air drawn in at *F*. This mixture passes through *G* to the cylinders of the engine, where it is exploded by a spark

"Antiknock" gasoline. As an explosion takes place suddenly, it is likely to produce a jarring, or "knocking," of the engine. This may be avoided by adding a small percentage of certain compounds to the gasoline. The most common of these "antiknocks" is lead tetraethyl ($Pb(C_2H_5)_4$), and gasoline containing a small percentage of lead tetraethyl and ethylene bromide ($C_2H_4Br_2$) is the well-known "ethyl gas."

The Diesel engine, the most efficient of all engines. Engines are very wasteful of energy. For example, if we could use all the energy contained in a gallon of gasoline, we could run a 3000-pound car, traveling at the rate of 30 miles per hour, 200 miles. Unfortunately, the gasoline engine uses only a small percentage of this energy. Even this is more efficient than the ordinary steam engine, which uses only from 6 to 8 per cent of the energy of the fuel consumed. The Diesel engine, now coming into such wide use, is the most efficient of all engines, giving back as much as 38 per cent of the energy of the fuel consumed. Even this is a most wasteful machine.

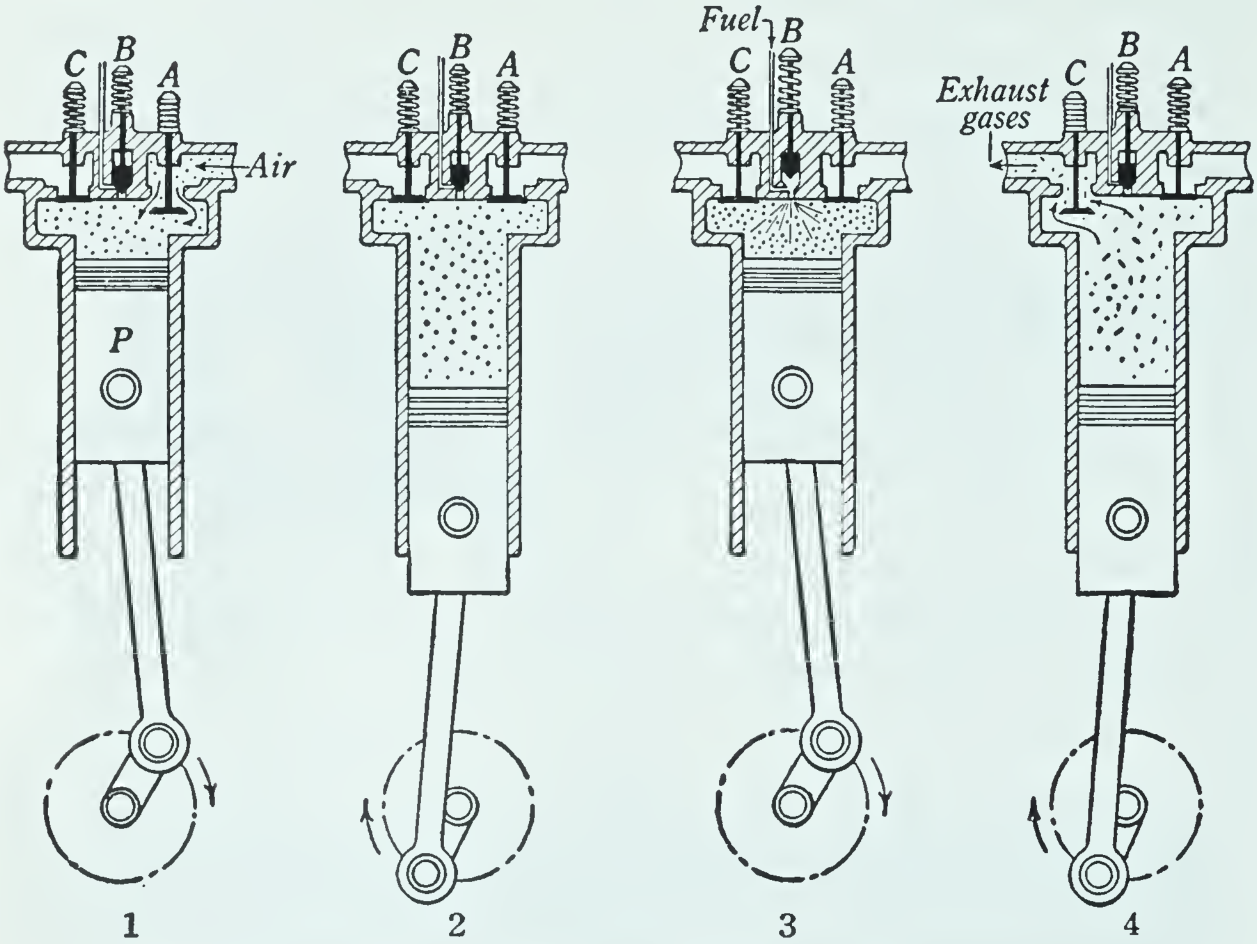


Fig. 336. Vertical section of the cylinder of a Diesel engine, showing the complete cycle of the piston

In section 1 the piston (*P*) is shown on its downward stroke, while air enters the cylinder through valve *A*. In section 2 the valve *A* is closed, while the piston moves upward, compressing the air and thus generating great heat. In section 3 the air has reached maximum compression. At this moment valve *B* opens long enough to allow a spray of oil to be forced into the cylinder. The temperature of the heated air is sufficient to ignite the oil. The hot products of the explosion push the piston downward. In section 4 valve *C* opens, allowing the exhaust gases to escape as the piston moves upward. The cycle is then repeated

In the Diesel engine, air alone is drawn into the cylinder on the downward stroke of the piston. The engine is so constructed that the air is compressed far more than is the explosive mixture in the ordinary gas engine. Now heat is evolved when a gas is compressed (Charles's law), and the more it is compressed the greater is the amount of heat evolved. In the Diesel engine the temperature of the air at its point of greatest compression in the cylinder is fully equal to that of a red-hot stove. At this point a fine spray of oil is forced into the cylinder, and the oil is at once ignited by the hot air. The high temperature resulting means that the molecules are moving with enormous velocity, and these, striking the head of the piston, push it downward (Fig. 336).

The electric furnace. In recent years electric furnaces have come into wide use for work at a very high temperature. Temperatures as high as 3500° can easily be reached by this means. These furnaces are based on one or the other of two general principles.

1. ***Arc furnaces.*** In this type the source of heat is an electrical arc formed between carbon electrodes separated a little way from each other, as shown in Figs. 332, 334. The substance to be heated is placed in a vessel, usually a graphite crucible, just below the arc.

2. ***Resistance furnaces.*** In the other type of furnace the heat is generated by the resistance offered to the current in its passage through poorly conducting materials. In its simplest form it may be represented by Fig. 333. The material to be heated, C, is placed between the ends of the electrodes E, E. Such furnaces are used in the manufacture of graphite (p. 140) and similar materials.

CHAPTER SUMMARY IN QUESTION FORM

1. Name (*a*) a solid fuel; (*b*) a liquid fuel; (*c*) a gaseous fuel.

2. (*a*) What is meant by the term *destructive distillation*? (*b*) Name four important products formed in the destructive distillation of coal.

3. (*a*) If you wished to manufacture coke, would you use the beehive ovens or the by-product ovens? (*b*) What conditions would determine your choice?

4. Prepare and fill out a table relating to the fuel gases, with the following headings:

NAME	CONSTITUENT GASES	RELATIVE HEAT VALUE	SOURCE

5. Name the relative advantages of each of the fuel gases.

6. What are the main products of combustion of each of the fuel gases?

7. How do we express the heat value (*a*) of gaseous fuels? (*b*) of solid fuels?

8. (*a*) What is the reason for speaking of smoke as a "nuisance"? (*b*) How can smoke be prevented?

9. Write the equation for the reaction that takes place in the manufacture (*a*) of water gas; (*b*) of producer gas.

10. (*a*) What conditions are necessary for producing a flame? (*b*) How do you account for the fact that a candle as well as a log of wood burns with a flame?

11. Make a diagram showing the three distinct parts, or regions, of a candle flame.

12. Which of the following statements is correct? The mixing of air with a fuel gas, as in the Bunsen burner, makes the flame hotter because (*a*) the flame is luminous; (*b*) the flame is non-luminous; (*c*) the combustion is complete.

13. Coal gas or acetylene issuing from a round pipe will burn, when ignited, with a luminous, smoky flame. (*a*) What makes the flame luminous? (*b*) Of what is the smoke composed? (*c*) How could you prevent the formation of smoke?

14. What name do we give (*a*) to the tip of a candle flame? (*b*) to the tip of the luminous cone of the flame?

15. (*a*) Name the reaction that occurs and the product formed when a metal is heated in that part of the flame referred to in (*a*), question 14. (*b*) Also name the change that occurs and the product formed when a metal oxide, such as lead oxide, is heated in that part of the flame referred to in (*b*), question 14.

16. To what is the force of an explosion due?

17. Name two causes of mine explosions.

18. Explain how a flame can be so protected that it will not ignite an explosive mixture of air and combustible gas when submerged in it. What name is given to the lamp so constructed?

19. Explain how gasoline makes an automobile go.

20. Name and describe the different kinds of electric furnaces.

THOUGHT QUESTIONS

1. (*a*) Why do we use a "choke" in starting an automobile? (*b*) Why do we use this device more in winter than in summer?

2. Why will an automobile not run well when "choked"?

3. We learned in Chapter X that 2 volumes of hydrogen combine with 1 volume of oxygen to form but 2 volumes of steam. Why, then, is a mixture of hydrogen and oxygen so explosive?

4. How do you account for the presence of nitrogen in (*a*) coal gas? (*b*) water gas? (*c*) producer gas?

5. (*a*) Is electricity a fuel? (*b*) Give reasons for your answer.

6. Suppose that in the manufacture of water gas you used 1000 lb of coke containing 90 per cent free carbon. (*a*) What weight of steam would be decomposed by this amount of carbon? (*b*) Determine, by inspection of the equation for the reaction, the relative volumes of the gaseous products formed.

OPTIONAL EXERCISES

1. (*a*) For every gallon of gasoline put into the tank of the average automobile, approximately 0.8 gal of water condenses from the exhaust pipe. Explain.

(*b*) Assuming that the average car travels 45,000 mi during its lifetime, with a gasoline consumption of 15 mi to the gallon, what volume of water would be formed in the combustion of the gasoline used?

2. Write to the Bureau of Mines, Washington, D.C., for papers on mine explosions, and report items of interest to the class.

UNIT READINGS

Beery. *Stuff*. [Chapter VI is entitled "Hot Stuff." It tells of petroleum and other fuels.]

Boyd. *Gasoline — What Everyone Should Know about It*. [Simple and interesting reading about this most important substance. Good pictures.]

Darrow. *The Story of Chemistry*. [Chapter IV, entitled "Chemistry and Power," tells about petroleum and other fuels.]

Egloff. *Earth Oil*. [A small book, well illustrated, that tells the story of petroleum in an interesting and popular way.]

Egloff. "Newer Products from Petroleum," *Journal of Chemical Education*, Vol. X, pp. 524–528. [Up-to-date information on this subject.]

Findlay. *Chemistry in the Service of Man*. [Chapter V treats of fuels and illuminants.]

Foster. *The Romance of Chemistry*. [Pages 362–378 tell about hydrocarbons and different fuel gases.]

Holmes. *Out of the Test Tube*. [Chapter XIX, "Fuels and Smoke," and Chapter XX, "Chemistry and the Motor Car," are brief and well worth reading.]

Tilden. *Chemical Discovery and Invention in the Twentieth Century*. [Pages 280–296 tell of petroleum. Good illustrations.]

The Science Leaflet. [No. 12 of recent volumes treats of organic compounds of carbon. In this number the student will find much of interest about hydrocarbons, petroleum, and gasoline.]

The World Book Encyclopedia. [Contains informative and well-illustrated articles on petroleum and natural gas.]

Unit Eleven. Some Important Compounds of Carbon: Organic Chemistry

THE inquiring student will wish to know something about the compounds found in our bodies, as well as in other living organisms, both plants and animals.

With the exception of water and calcium phosphate, nearly all compounds found in living organisms contain carbon. There are a great many of these; about 30,000 are thought to be present in the different organisms. In addition to these, many thousands of other carbon compounds are known, most of which have been built up in our laboratories. That great branch of chemistry called *organic chemistry* has to do with the study of all these carbon compounds.

The early chemists limited the term *organic chemistry* to the study of those carbon compounds present in living organisms. They believed that these could be built up only through the action of what they called the *vital force* or *life* of the organism; they thought it impossible to make them in the laboratory. The great German chemist Wöhler, in 1828, was the first to disprove this idea, for he was able to prepare in the laboratory the white crystalline compound called urea — a compound present in the human body. Following this discovery and others like it, the term *organic chemistry* was extended to include all carbon compounds, no matter where found or how made.

We have already studied one group of carbon compounds, the hydrocarbons. In this unit we shall turn our attention to a few of the many others of importance in our everyday life. This will take us into a study of such materials as foods, medicines, textiles, paper, soaps, and dyes.

CHAPTER XXXIX

Some Important Organic Compounds

[Compounds That Make Life Possible]

Groups of organic compounds. At present there are perhaps three hundred thousand organic compounds known, and new ones are being discovered almost daily. Fortunately these fall into natural groups, or families, just as the elements do. The compounds belonging to each group have similar compositions and properties, and so we may study the properties of the group as a whole rather than the special compounds. We can consider only a few of the most common groups, and these very briefly. We shall begin with the group called the carbohydrates.

I. THE CARBOHYDRATES

What is a carbohydrate? Whether we have known it or not, we have depended on the carbohydrates all our lives. Some of them, like the sugars and starches, are part of our daily food. Cellulose, another important carbohydrate, makes up the fibers from which much of our clothing is woven, and is the raw material in the manufacture of such common things as paper, photographic films, and most of our explosives.

Although the carbohydrates are so abundant and important, it is not easy to define these compounds. The best we can do is to say that the group word *carbohydrate* includes the sugars, starches, and cellulose; that all of these contain nothing but carbon, hydrogen, and oxygen; and that in nearly all the carbohydrates the hydrogen and oxygen are present in the same ratio as in water, namely, 2 atoms of hydrogen to 1 of oxygen. We shall begin our study of the carbohydrates with the sugars.

Sucrose (ordinary sugar) ($C_{12}H_{22}O_{11}$). There are many sugars, but *sucrose* is the common one we buy at the grocer's and use to sweeten our foods. It is found in many plants, but the world's supply comes from sugar cane and sugar

FIG. 337. Source of the world's output of sucrose — the sugar cane and the sugar beet

beets (Fig. 337). Sugar cane grows only in warm climates (Cuba is the chief producer), while sugar beets thrive in cooler climates, such as prevail in Colorado and Nebraska. We speak of *cane sugar* and *beet sugar* simply to name the *source of the product.* It is the same product from either source, although many housewives think differently.

How we get pure sugar. The juice from the sugar cane or sugar beet contains the sucrose along with many impurities. These are removed by treatment with various chemicals, and the resulting solution is then evaporated until the sucrose crystallizes. The evaporation is carried out in large covered pans from which the air has been partly removed (Fig. 338). This is to lower the boiling point of the solution and so prevent the charring of the sucrose. The crystals are separated from the liquid by whirling the mixture at high speed in perforated vessels called centrifugals (Fig. 339).

The liquid that remains when cane-sugar crystals have been removed is a common form of *molasses.* Brown sugar is partially purified cane sugar. Any impurities remaining in beet sugar give it an unpleasant taste; so beet sugar must be highly refined. *Maple sugar*, obtained by evaporating the sap of the maple tree (Fig. 342), also consists of sucrose. Its

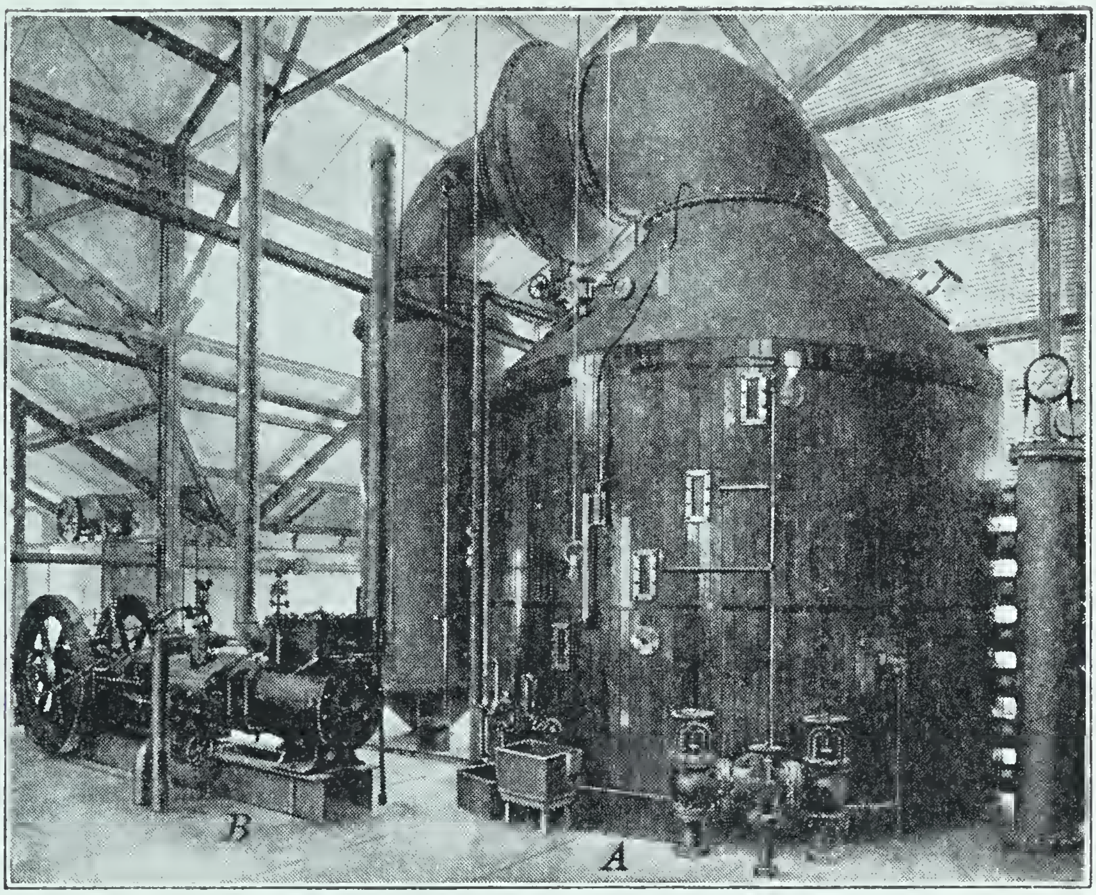


FIG. 338. Vacuum pans in a sugar factory

The air is pumped from the large covered pans *A* by the engine ***B***

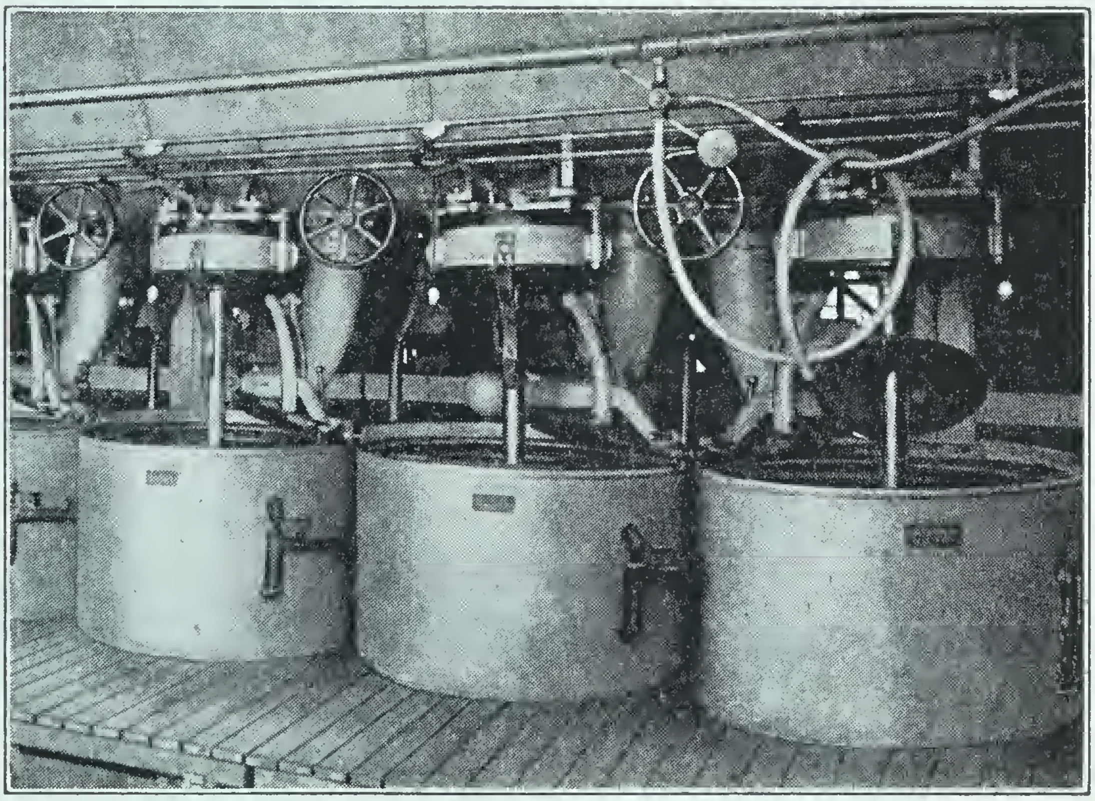


FIG. 339. Centrifugals for separating the sugar from sirup

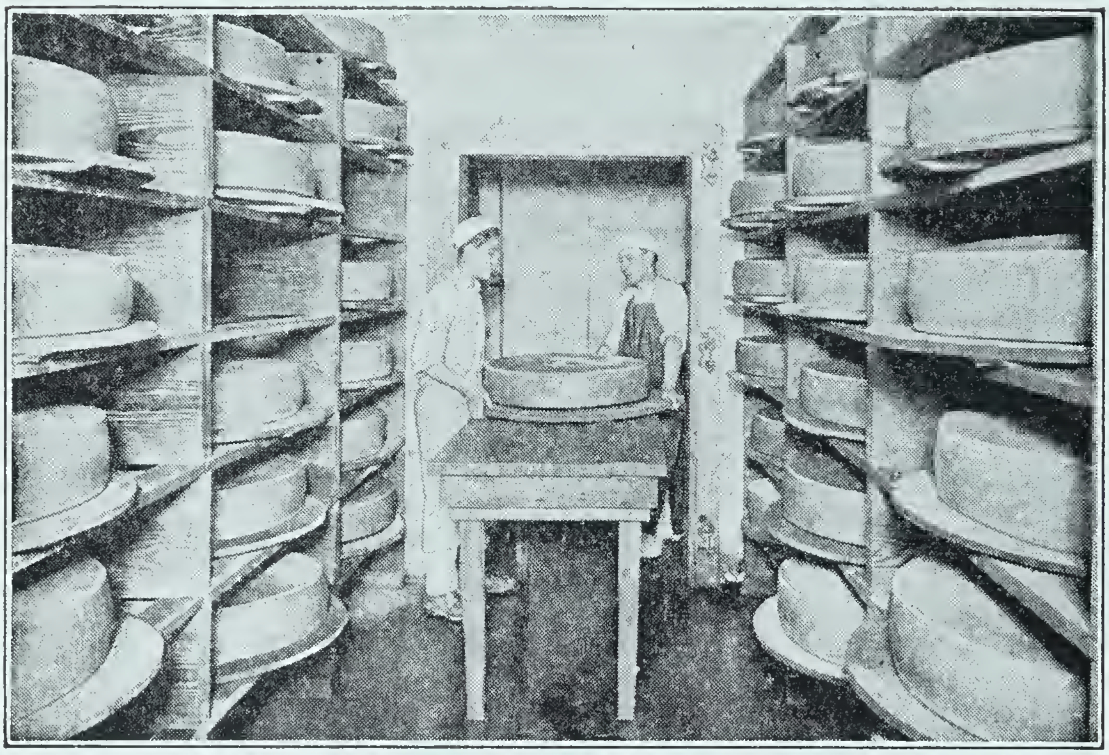


Fig. 340. Cheese stored for "ripening"

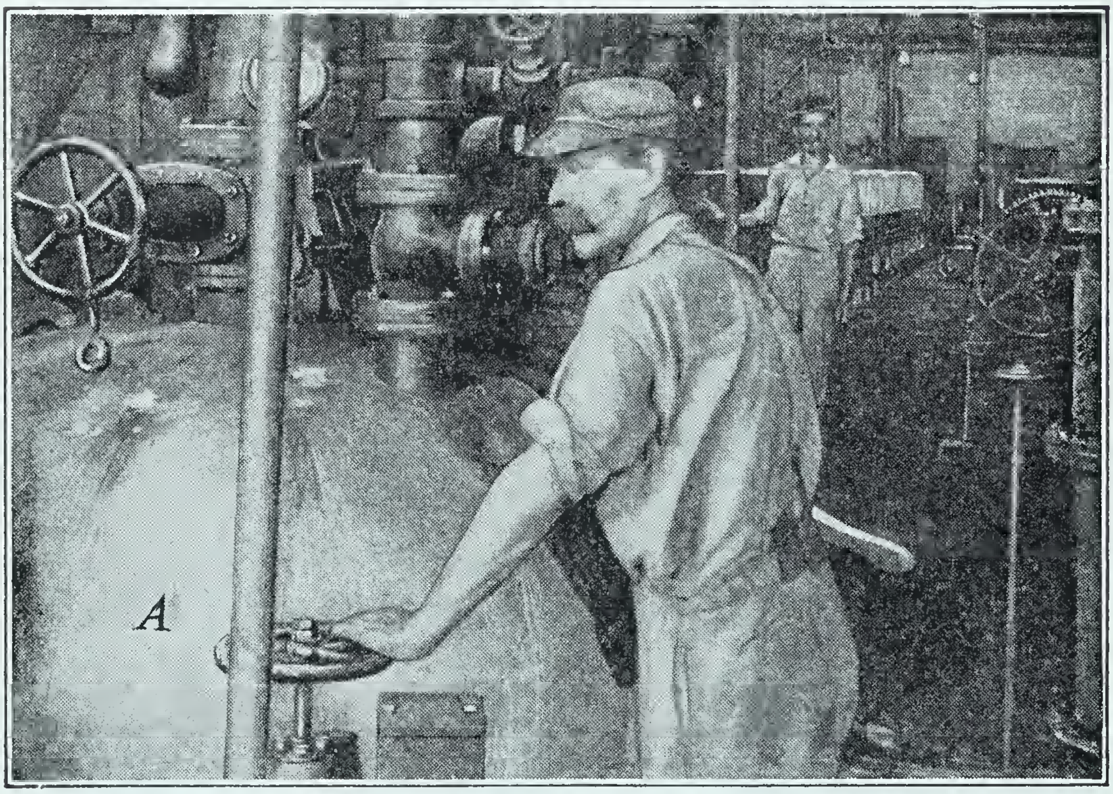


Fig. 341. Making glucose (corn sirup)

Starch and a little hydrochloric acid are heated with steam in a large copper vessel *A*, which is known as a "converter"

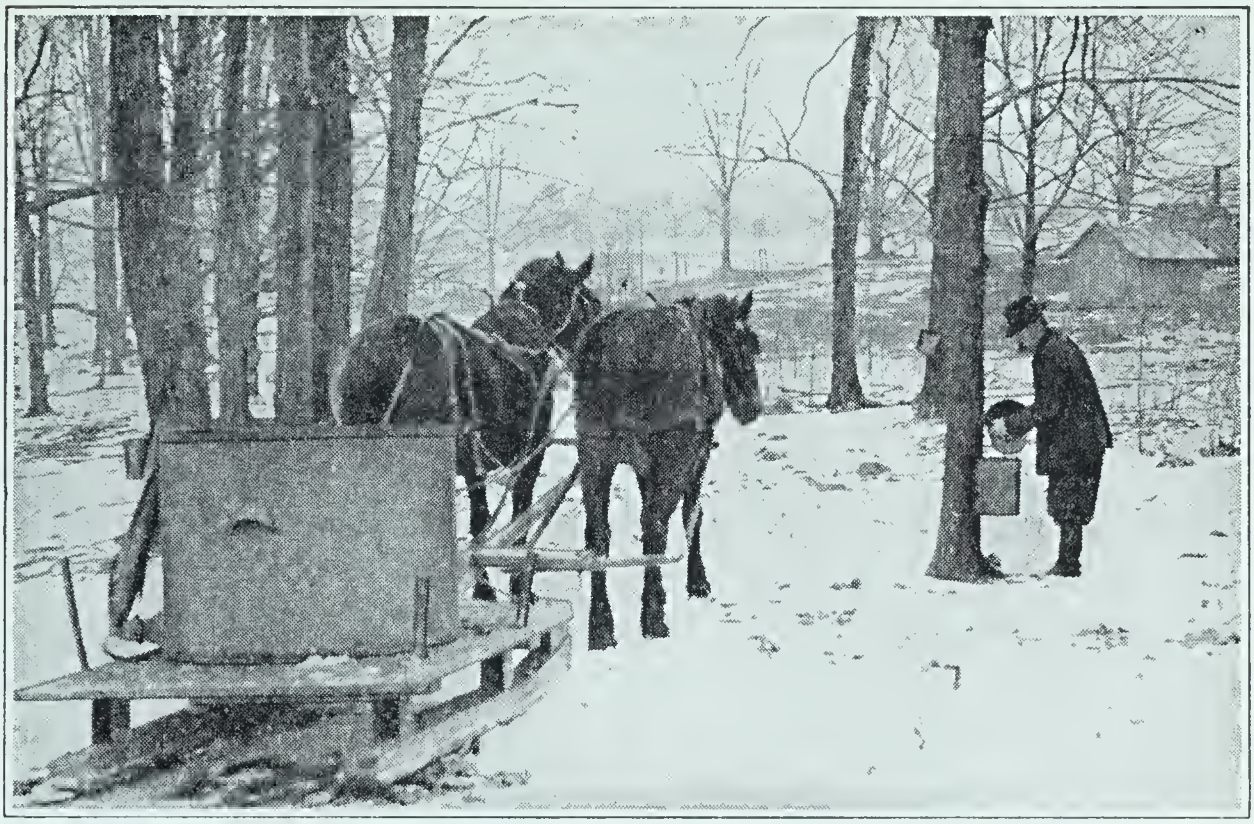


FIG. 342. A maple-sugar camp

In the spring the maple trees are tapped, and the sap that flows out collects in buckets attached to the trees. When evaporated, this sap yields either maple sirup or maple sugar, depending on the extent of the evaporation

distinctive flavor is due to the presence of small percentages of certain other compounds in the maple sap.

The amount of sugar consumed annually in the United States averages about one hundred pounds for each inhabitant. Someone has expressed it less accurately by saying that, on the average, each one of us eats his own weight of sugar yearly.

Chemical conduct of sucrose. When a solution of sucrose is heated to about 70° with dilute hydrochloric acid (which acts as a catalyst), the sucrose and water react to form the two simpler sugars *dextrose* and *levulose,* each of which has the formula $C_6H_{12}O_6$.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{dextrose}}{C_6H_{12}O_6} + \underset{\text{levulose}}{C_6H_{12}O_6}$$

In this reaction the sucrose is said to undergo *inversion,* and the mixture of equal parts of dextrose and levulose formed is called *invert sugar.*

When sucrose is heated to about 215°, a partial decomposition takes place, and a brown substance results called *caramel.* This is used as a coloring matter in making confectionery.

Different compounds may have the same formula: isomeric compounds. The thoughtful student will wonder how it can be that the two sugars, dextrose and levulose, mentioned in the preceding paragraph have the same formula. The reason is that the properties of a compound depend not only on the elements composing it but even more on how the atoms are arranged in the molecule. While the molecules of dextrose and levulose are each made up of the same number of atoms of carbon, hydrogen, and oxygen, these atoms are arranged in one way in the molecule of dextrose and in a different way in the molecule of levulose, just as the checkers on a checkerboard may be arranged in two (or more) different ways. *Compounds that have the same molecular formulas are said to be isomeric compounds.*

The sugar that makes milk sweet; lactose (milk sugar) ($C_{12}H_{22}O_{11}$). This sugar resembles sucrose in appearance, but it is not as soluble and is only about one fourth as sweet as sucrose. It is present in the milk of all mammals. The average composition of fresh cow's milk is as follows:

Water	87.0%
Nitrogen compounds, chiefly casein	3.5%
Butter fat	3.9%
Lactose	4.9%
Mineral matter	0.7%

The butter fat is present in the form of small globules dispersed through the water or as an emulsion. When the milk is set aside, the emulsion breaks down, and the fat droplets run together into large drops lighter than water; we say that the cream rises to the top.

The souring of milk is caused by microscopic plants having the general name *bacteria*. These plants, as well as the spores and seeds that produce them, are very abundant in the air, in dust and dirt, and so easily get into the milk. Since the milk is a good food for them, they increase rapidly and, in some way not well understood, change the milk sugar into *lactic acid*, a sour liquid that has the formula $C_3H_6O_3$. In this change the milk sugar is said to undergo *lactic fermentation.*

$$\underset{\text{lactose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow 4\ \underset{\text{lactic acid}}{C_3H_6O_3}$$

The souring of milk can be prevented or, at least, delayed by extreme cleanliness, which helps to keep the bacteria from getting into the milk; also by heating the milk to about 65° for forty minutes. The heat kills at least most of the bacteria present. Milk heated in this way is said to be *pasteurized.* This word recalls the name of the great French scientist Pasteur (Fig. 343), who first proved that fermentations as well as many diseases are due to minute organisms.

FIG. 343. Louis Pasteur (1822–1895)

A great French scientist, famous for his work on fermentation and the cause and prevention of contagious diseases

The composition of cheese, and how it is made. When milk sours, the lactic acid formed causes the casein of the milk to separate in solid form, and we say that the milk *curdles.* The casein can also be made to separate by adding to the milk a substance known as *rennet* (Fig. 344), obtained from the lining of calves' stomachs. This is the first step in the making of cheese. The casein, as it separates, carries with it most of the butter fat and mineral salts present in the milk. This mixture of casein, butter fat, and mineral salts is removed by filtration, and is then salted, compressed into molds, and stored under varying conditions (depending upon the kind of cheese desired) in order to *ripen* (Fig. 340). During this process a number of reactions take place, making compounds that give the cheese its distinctive flavor. Each of these reactions is caused by some special

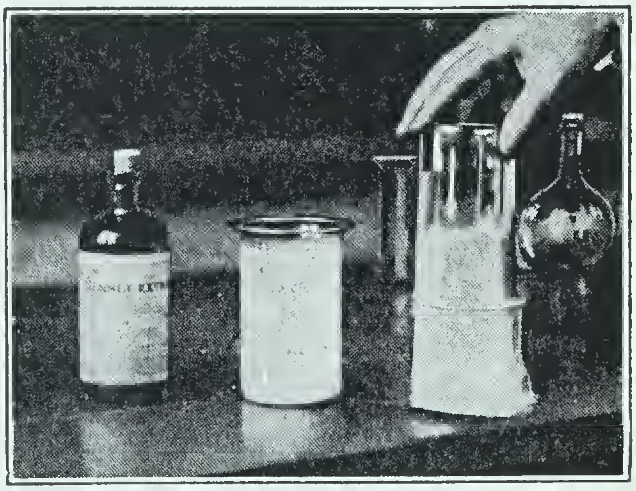


FIG. 344. When rennet is added to milk, the casein separates (or sets) as a porous solid

micro-organism which is added to the casein mixture. Different organisms produce different flavors, and so make different kinds of cheese.

Dextrose, the cheapest but not the sweetest of the sugars ($C_6H_{12}O_6$). This sugar has a number of names. It is called *grape sugar* because of its presence in grapes, and *corn sugar* because it is commonly prepared from cornstarch. It is also known as *glucose*, though, of course, it has no relation to glue. It occurs in honey and in many fruits and vegetables. It is also present in small amounts in our bodies, and in much larger amounts if we are afflicted with the disease called diabetes.

While we can get dextrose from grapes and other fruits, it is much cheaper to make it by heating starch with water containing a small percentage of hydrochloric acid (which acts as a catalyst). If this action is carried to completion, pure dextrose results. If it is but partly completed, a thick sirup containing dextrose, dextrin (p. 462), and maltose (p. 471) results. This sirup is called *commercial glucose* or, more often, *corn sirup*, since the starch from which it is prepared is commonly obtained from corn:

$$\text{starch} \xrightarrow{H_2O + HCl} \text{corn sirup} \xrightarrow{H_2O + HCl} \text{dextrose}$$

Corn sirup is prepared in enormous quantities by heating starch, water, and acid together in large copper retorts (Fig. 341). When the reaction has gone far enough, the acid is neutralized with sodium bicarbonate (baking soda).

Glucose is much cheaper than sucrose, but is only about half as sweet. It is used as a constituent of such foods as candy, jellies, jams, and table sirups.

Levulose, the sweetest of sugars ($C_6H_{12}O_6$). This sugar, also called fructose and fruit sugar, occurs in honey and in various fruits along with dextrose and sucrose. It is a good food, sweeter even than sucrose, and undoubtedly would be widely used if some cheap method of production could be found.

Starch, one of the most widely distributed of the carbohydrates ($(C_6H_{10}O_5)_x$). As we have seen, the formula of a compound gives the composition of its molecule. To find the

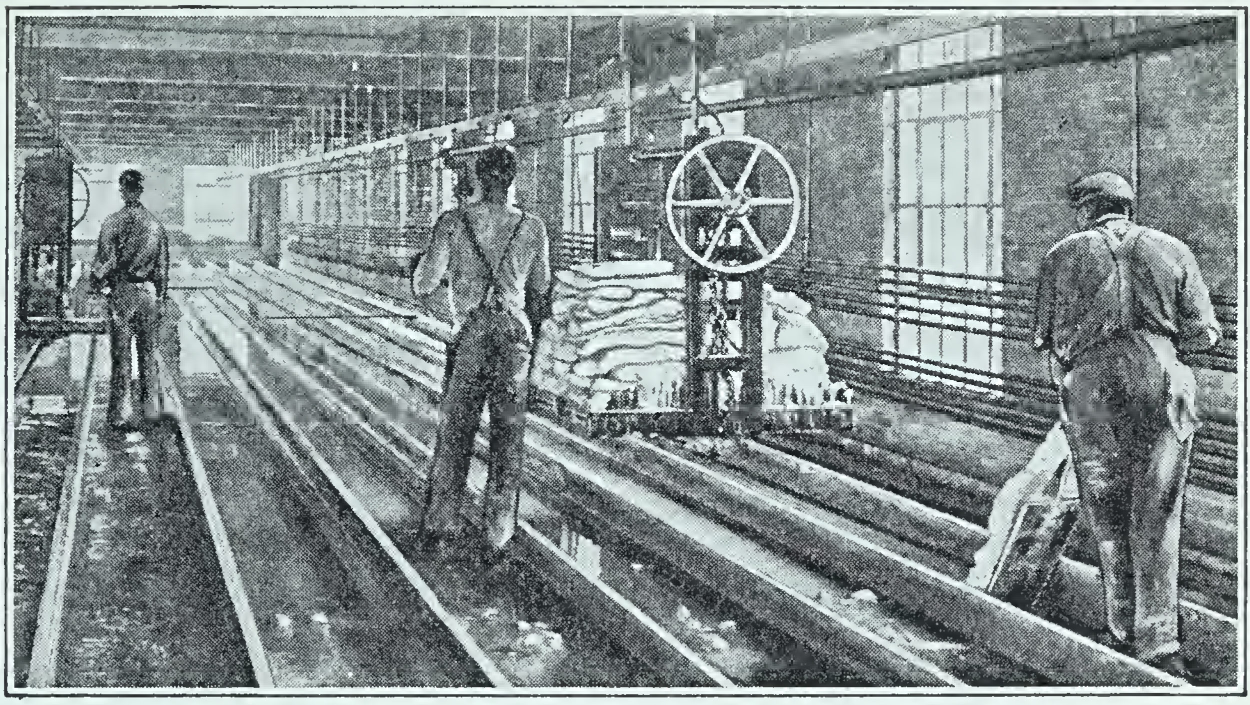


FIG. 345. Settling troughs in a starch factory

The ground corn or potato, suspended in water, flows slowly through long troughs. The starch settles to the bottom, while lighter materials, such as the seed germ, hulls, and pulp, float off at the end. After the troughs are drained, the starch is removed with shovels

real formula of a compound, we must know its molecular weight. But starch is an insoluble solid, and the molecular weight of such a compound cannot be measured (p. 181).

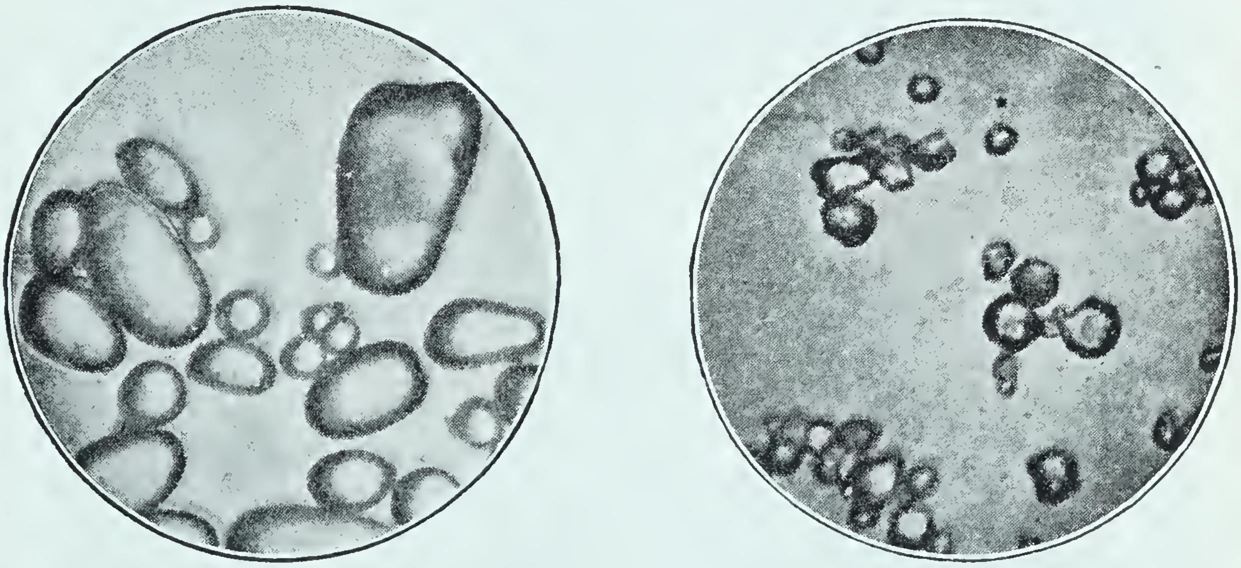
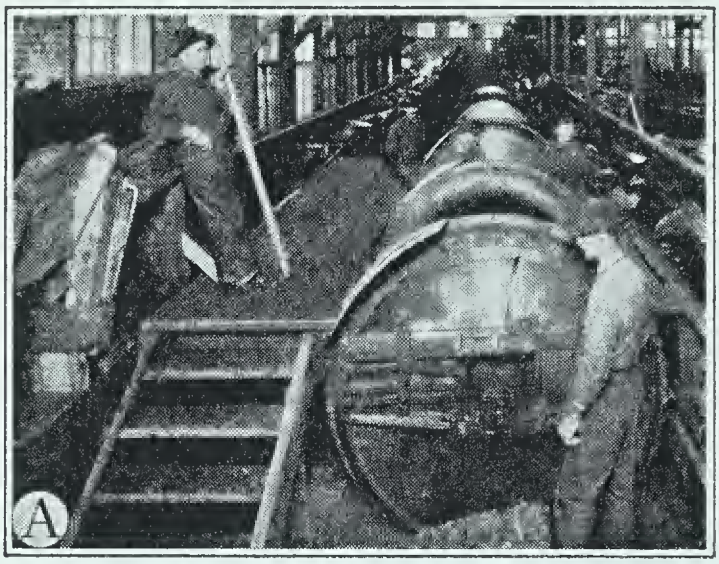


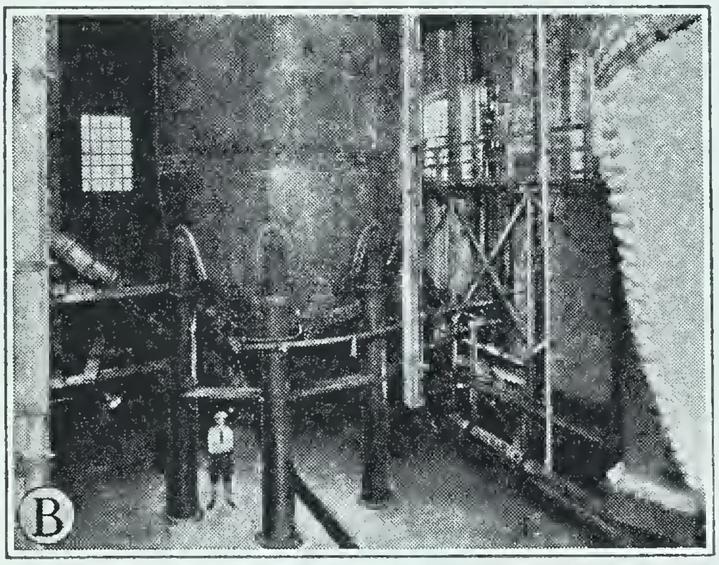
FIG. 346. Granules of wheat starch (at left) and of corn starch (at right) (magnified 290 times)

However, we do know that it is some multiple of the simple formula $C_6H_{10}O_5$; so we write its formula $(C_6H_{10}O_5)_x$, in which x is the unknown multiple.

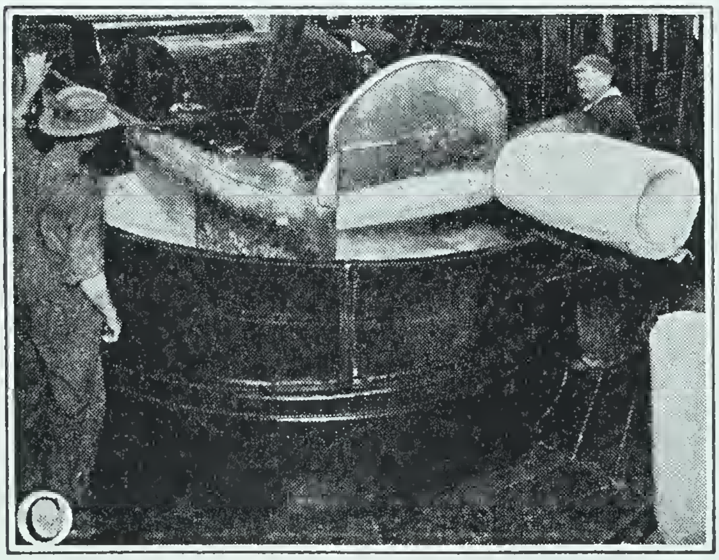
Starch seems to be excess food stored up for the plant, and is present chiefly in roots, tubers, and seeds. On the average



The logs are cut into pieces, and the bark and other undesirable parts removed. The pieces are then run into the "chippers," which cut hundreds of cords of wood daily into small chips about the size of a domino



The chips are then run into huge cylinders and heated for several hours with chemicals that dissolve the undesirable materials, leaving the pure cellulose. This is then washed and bleached, forming the paper pulp



The cellulose fibers must next be separated from each other, and soaked and filled with water. This is done by "beating engines" that separate the fibers without breaking or injuring them

Fig. 347. A, B, C. Some steps in the manufacture of paper

Courtesy of the Champion Coated Paper Company

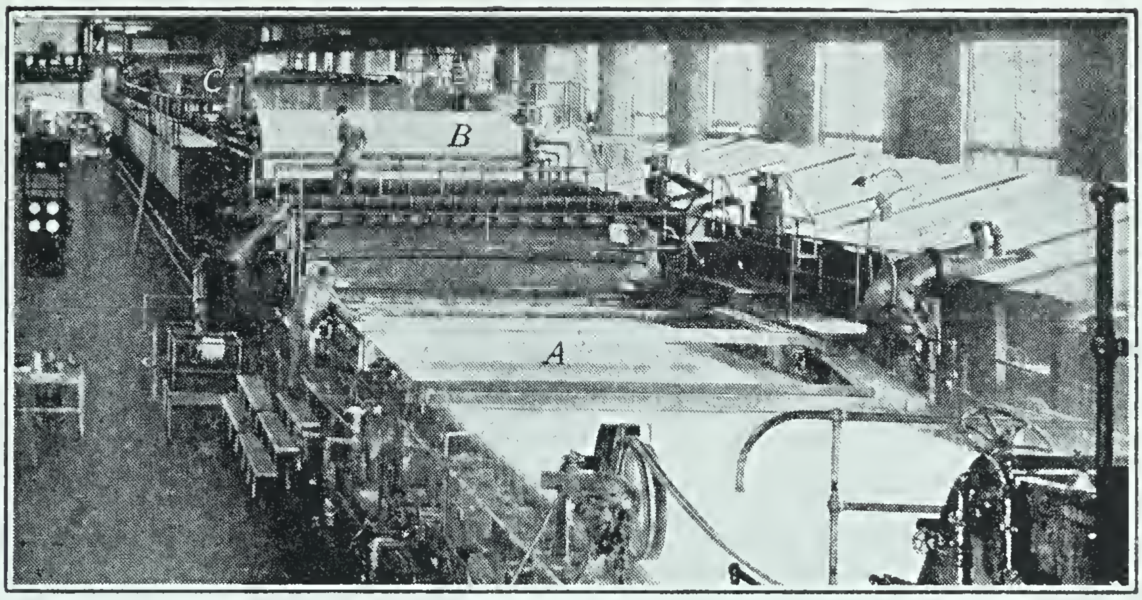


Fig. 348. View of one type of paper machine

The mixture of paper pulp, added material (such as clay, starch, or resin, according to the kind of paper), and water is run onto a traveling belt of wire cloth (*A*). Most of the water present drains through the wire, leaving the fibers in the form of a felted sheet which constitutes the paper. The sheet is then passed through a series of presses carried on endless woolen belts (one is shown at *B*) to remove still more of the water present. The sheet then leaves the woolen belts and is carried around a number of large metal cylinders (*C*), heated by steam, to dry the paper. (Courtesy of the International Paper Company)

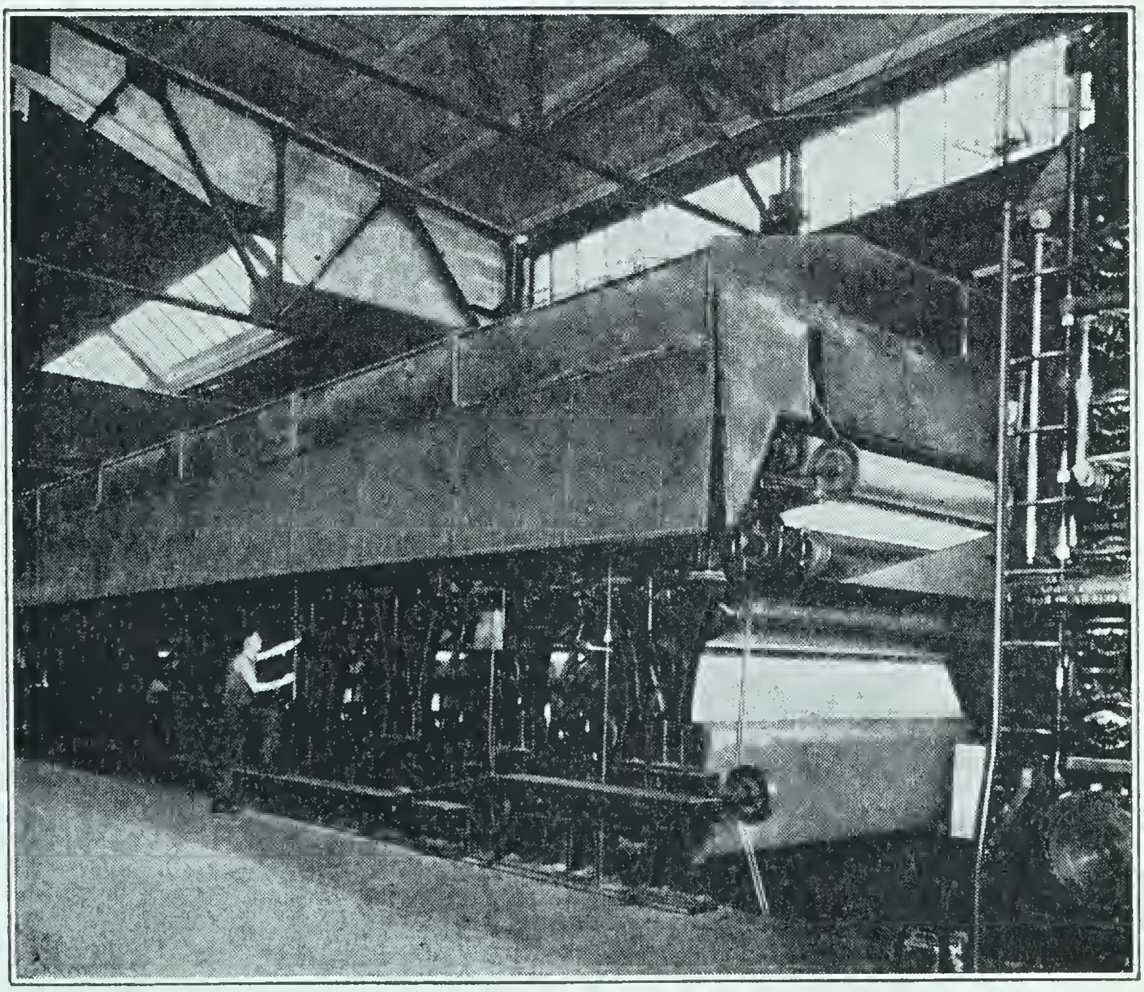


Fig. 349. This picture shows the sheet as it leaves the last set of dryers. It is then practically completed paper, ready for further surfacing if so desired

Courtesy of the Champion Coated Paper Company it makes up more than half of the cereal grains and potatoes. In the United States, starch is obtained chiefly from corn, about 70 per cent of which is starch. In Europe the potato is its principal source. It is made by grinding the corn or potato finely and then parting the starch from the other materials by taking advantage of its greater density, as explained in Fig. 345.

Starch is made up of minute granules, which differ somewhat in appearance according to their source (Fig. 346), so that it is usually possible to tell the source of a sample by examining it under the microscope. When heated with water, these granules burst, and the starch partially dissolves; so starchy foods become more digestible by cooking. When roasted under proper conditions, starch is changed into a soluble carbohydrate called *dextrin.* This is used in making pastes and mucilage, such as are used on the back of postage stamps.

Cellulose $(C_6H_{10}O_5)_x$, the solid framework of most plants. As with starch, the molecular weight of cellulose is unknown, but it is some multiple of the simple formula $C_6H_{10}O_5$. So we write its formula $(C_6H_{10}O_5)_x$.

Cellulose itself, or more often some derivative of it, is present in all plants. Cotton fiber contains about 91 per cent of nearly pure cellulose, while ordinary woods contain from 40 to 60 per cent either of cellulose or of some of its derivatives. Pure cellulose can be got from plants by treatment with appropriate reagents, and its properties are much like those of the better grades of filter paper, which are nearly pure cellulose. It is an inactive compound, and is insoluble in all ordinary solvents, although it is readily changed into soluble derivatives. When heated with concentrated hydrochloric acid, it unites with water, forming dextrose:

$$\underset{\text{cellulose}}{(C_6H_{10}O_5)_x} + x\,H_2O \longrightarrow x\,\underset{\text{dextrose}}{C_6H_{12}O_6}$$

Cellulose is the principal material used in the manufacture of (1) paper, (2) cotton and linen cloth, (3) rayon and cellophane, and (4) the widely used cellulose nitrates. These will now be briefly described.

How paper is made. Paper consists mainly of vegetable fibers (cellulose) so interwoven as to form a continuous flat surface. The finer grades are made chiefly from bleached cotton rags, but the greatest quantity (newsprint paper) is made from *wood pulp*, which is composed of the fiber of wood. Canada leads all other countries in the production of wood pulp.

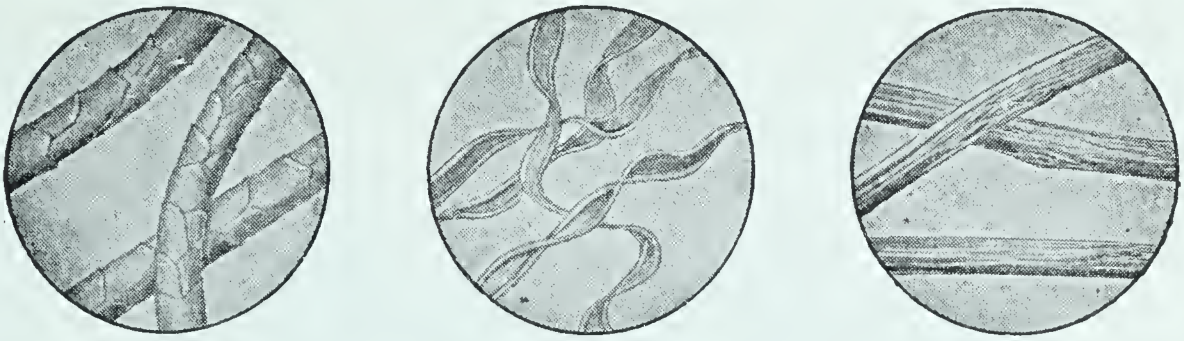

Wool fiber Cotton fiber Silk fiber

FIG. 350. Textile fibers (highly magnified)

Different methods are used in making paper, but the principal one is shown very briefly in Figs. 347, 348, and 349.

How the textile fibers differ from each other. The cloth from which our clothes are made is woven from yarns made of fibers obtained from various sources. The *vegetable* fibers — cotton, obtained from the cotton plant, and linen, made from flax and hemp — are chiefly cellulose. The *animal* fibers — wool and silk — are composed of complex compounds of nitrogen. To the naked eye all these fibers look very much alike, but when they are examined under the microscope their appearance differs widely. In this way we can easily tell the source of any particular fiber (Fig. 350), and whether the silk necktie we may have bought is really silk or simply a cheaper material made to look like silk.

Silk. Silk has long been known and highly prized. It is often mentioned in the Bible. The silk fiber is spun by silkworms, which are grown in large numbers for this purpose, especially in Japan and China. But silk is expensive, and an effort has long been made to get a cheaper material that will have the properties of the natural product. This has led to the manufacture, in enormous quantities, of a form of artificial silk to which the name *rayon* has been given.

Rayon. Rayon is a form of cellulose, while real silk is composed of compounds of nitrogen; so, although the two look alike, it is easy to distinguish between them. Rayon is made from cellulose obtained partly from cotton and partly from spruce wood. The common method of making rayon is shown in Figs. 351 and 352. The United States produces many millions of pounds annually.

Nylon. After years of research, this textile has been developed and has come into large use. It is a nitrogenous product and resembles silk in both composition and appearance; indeed it can be made finer and stronger than silk. Produced in the form of a fiber, it has all the uses of silk. In coarser forms, it is used in making bristles for brushes. The source materials from which it is made can all be obtained from coal, limestone, air, and water.

Cellophane; mercerized cotton. The common wrapping material called *cellophane* has the same composition as rayon and is made in the same way, except that the cellulose solution (viscose) is forced into the hardening bath through a narrow slot, thus making thin sheets rather than threads of cellulose.

Another form of cellulose that has a silklike appearance is known as *mercerized cotton.* It is made by treating cotton cloth, stretched to prevent shrinkage, with a cold concentrated solution of sodium hydroxide.

Cellulose nitrates, commonly called nitrocellulose, are explosive, but have many peacetime uses. While we do not know the exact formula for cellulose, we do know that its molecule contains a number of OH groups. When nitric acid (mixed with a little sulfuric acid to assist in the reaction) acts on cellulose, one or more of the OH groups is replaced by an equal number of NO_3 groups. The number of OH groups so replaced depends on the conditions under which the reaction is carried out, such as the strength of the acid and the duration of the reaction. Ordinarily we do not obtain one single compound but a mixture of several.

Now just as the compound formed by the action of nitric acid on sodium hydroxide is called sodium nitrate, so the compounds formed by the action of nitric acid on cellulose are called *cellulose nitrates.* The mixtures of these nitrates have a number of common names. For example, we call the

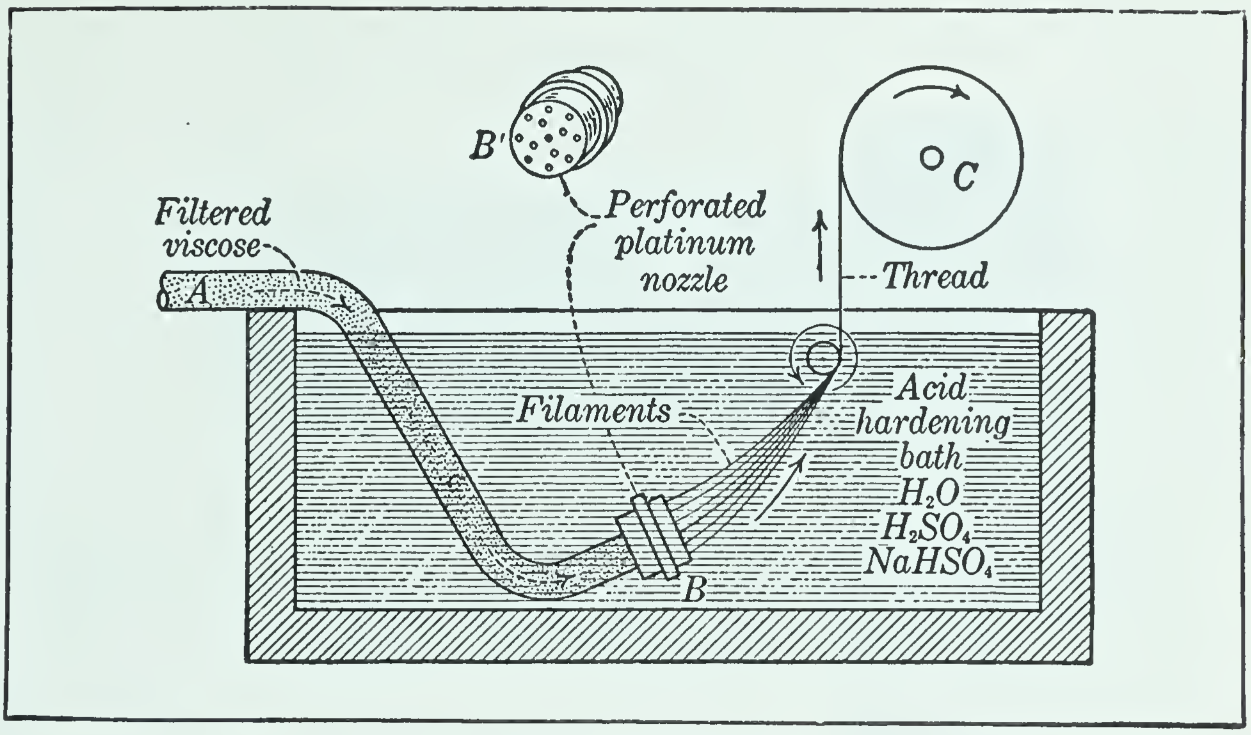

B'
Filtered viscose
A
Perforated platinum nozzle
C
Thread
Filaments
Acid hardening bath
H_2O
H_2SO_4
$NaHSO_4$
B

FIG. 351. Making rayon threads

Pure cellulose is treated first with sodium hydroxide and then with carbon disulfide, producing a product that forms a colloidal dispersion in a dilute solution of sodium hydroxide. This liquid, known as *viscose*, *A*, is filtered and then forced through a perforated nozzle, *B*, *B'*, and emerges into the hardening bath in the form of fine threads. These are twisted into a coarser thread and wound on the reel *C*

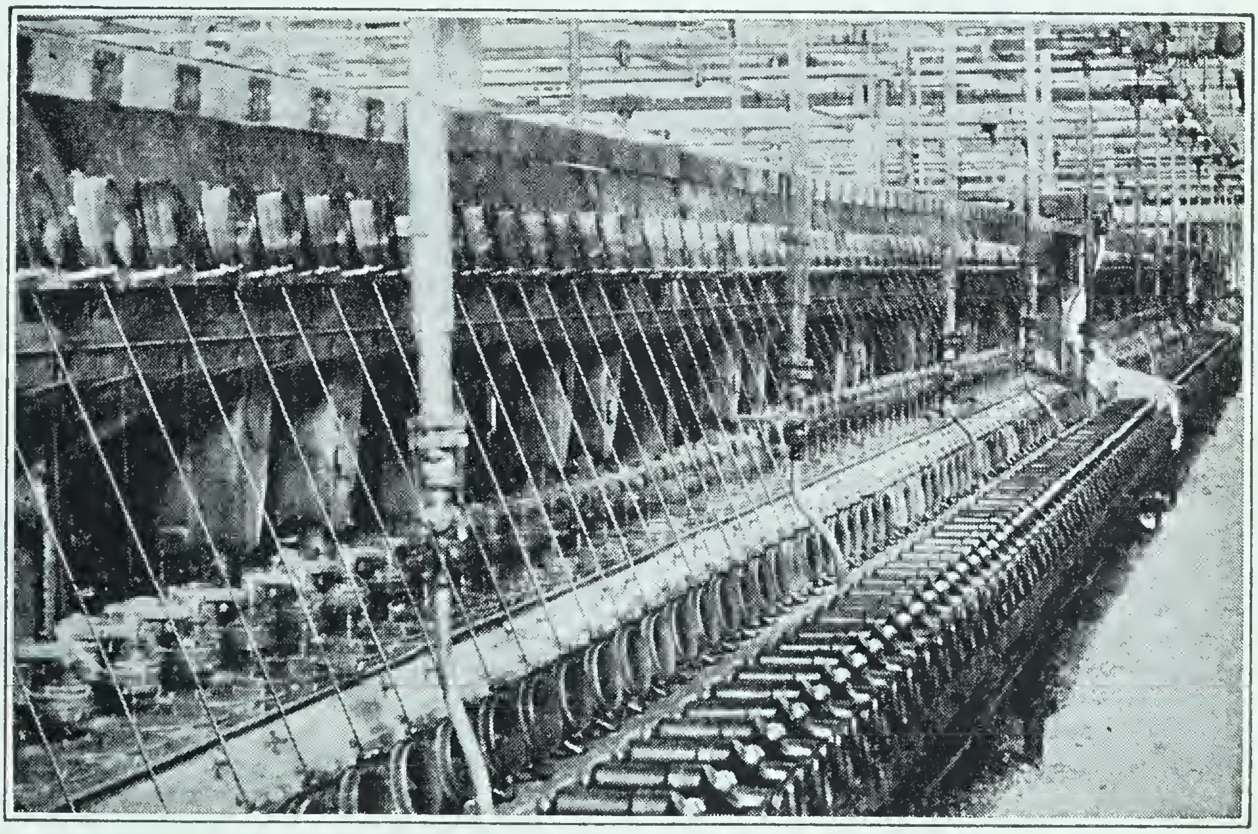


FIG. 352. View in a rayon factory where the processes described in FIG. 351 are being carried out

The rayon threads are seen as they emerge from the hardening bath. They are twisted into coarser threads, and these are wound on reels

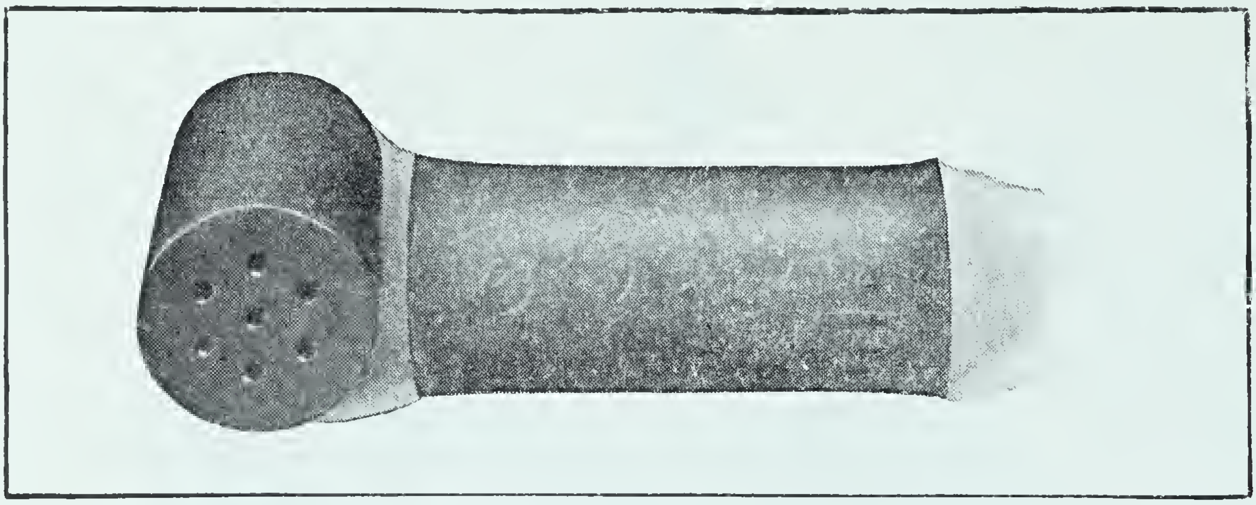


FIG. 353. Grains of smokeless powder (approximately natural size) for large guns. Smokeless powder is made of nitrocellulose

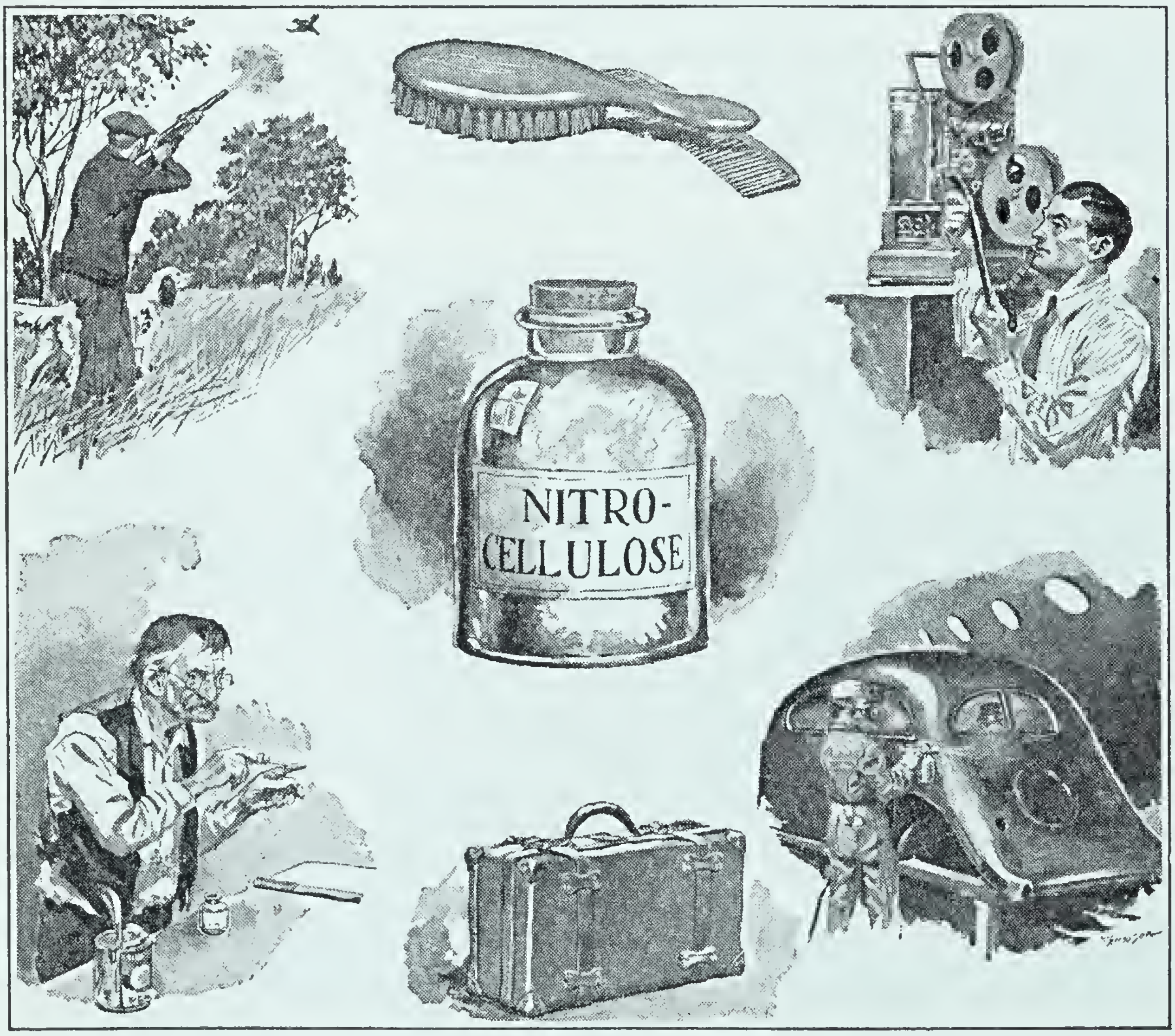


FIG. 354. Some uses of nitrocellulose

The pictures show a number of articles, all or parts of which are made from nitrocellulose. Indicate the product used in each picture mixtures of the nitrates containing a small number of NO_3 groups *pyroxylin*, while those made up of nitrates containing a larger number of these groups are called *guncotton.* Pyroxylin also differs from guncotton in being soluble in a mixture of alcohol and ether (p. 470). All these nitrates are white solids, but we can also get them in transparent form, as is true of photographic films and cellophane. They are inflammable, and guncotton under certain conditions is highly explosive.

What are the uses of nitrocellulose? The importance of nitrocellulose is shown by the following uses: (1) it is the chief constituent of *smokeless powders* for guns (Fig. 353); (2) *photographic films* are made from the transparent form, also from a similar compound known as *cellulose acetate* (Fig. 355); (3) it is the basis of the *lacquers* now so widely used under many trade names, especially for painting automobiles; (4) it is an important constituent of many varieties of *artificial leather*; (5) *collodion*, which we buy from the druggist and use in place of court plaster, is a solution of nitrocellulose in a mixture of alcohol and ether; (6) *celluloid* is a mixture of nitrocellulose and camphor (or some similar material), often colored by a wide variety of dyes.

Fig. 355. Section of movie film made of cellulose acetate

It should be kept in mind that nitrocellulose is highly inflammable and therefore that articles (such as hair combs) made from it are likely to burn readily. Many serious accidents have resulted from the careless use of these articles.

Where do the carbohydrates found in plants come from? Many scientists have tried to find out how the carbohydrates present in plants are formed, but as yet the problem is only partly solved. They must be formed by some process, and we call this process *photosynthesis*. But this name tells only that light is required for their formation.

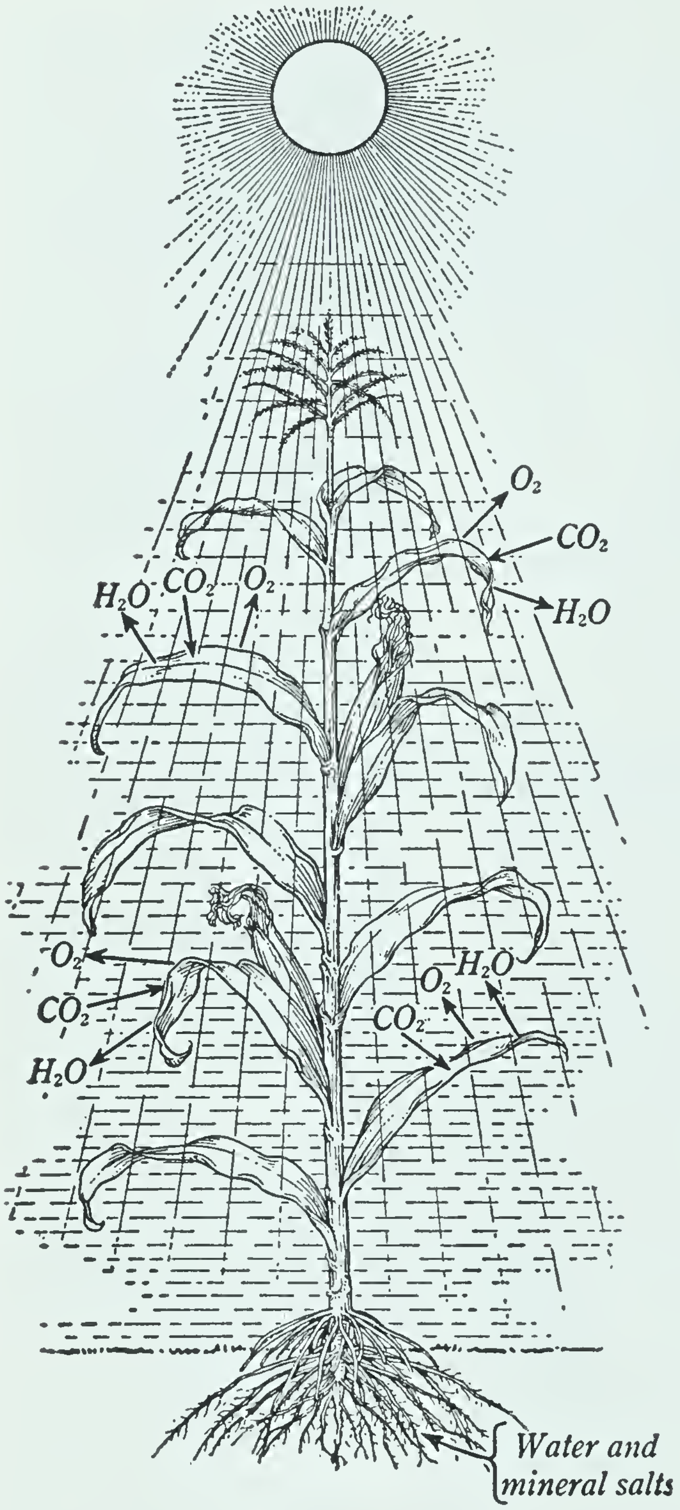


FIG. 356. Photosynthesis

The plant builds up (or synthesizes) carbohydrates, using water, mineral salts, and some carbon dioxide taken from the soil, and carbon dioxide from the air. Oxygen is set free in the process. The sunlight furnishes the energy that is required in the building-up process

So far as we know at present, the following are true statements about the formation of the plant carbohydrates: (1) they are formed only in green plants; (2) the raw materials used are carbon dioxide from the air, and water from the soil, oxygen being set free in the process; (3) sunlight is necessary to supply the needed energy (Fig. 356); (4) the complex magnesium compound known as *chlorophyll*, which is present in all green plants, plays a necessary part; (5) certain minerals must be in the soil in which the plant is grown.

Dextrose, it seems, is the first carbohydrate to be formed, the others being made from it. The reaction for the formation of dextrose is generally expressed by the equation

$$6\ CO_2 + 6\ H_2O \longrightarrow C_6H_{12}O_6 + 6\ O_2\uparrow$$

This equation tells us that dextrose and free oxygen are formed, but it does not tell the part played by the chlorophyll and mineral salts; indeed, we do not know how they act.

SUMMARY OF PART I OF CHAPTER IN QUESTION FORM

1. (*a*) Define the term *carbohydrate.* (*b*) What fact suggested the name? (*c*) How do the carbohydrates differ from the hydrocarbons in composition?

2. Prepare a table containing information relating to each of the important sugars, under the following heads:

Chemical Name	Common Name	Chief Source	Uses

3. (*a*) Write the equation for the reaction that takes place when sucrose is heated with water and hydrochloric acid. (*b*) Give the name of each of the compounds formed; (*c*) also the name given to the mixture of these compounds.

4. What name is given to a coloring matter, made from sucrose, that is used in making confectionery?

5. The formula $C_6H_{12}O_6$ may represent either dextrose or levulose, two entirely different sugars. (*a*) What name do we give to different compounds which have the same formula? (*b*) How do we account for the fact that two (or more) different compounds may have the same formula?

6. To what is due (*a*) the sweet taste of fresh milk? (*b*) the sour taste of milk that has stood for some time?

7. (*a*) What causes the souring of milk? (*b*) Why does it sour more readily in hot weather than in cold? (*c*) How can the souring be delayed? (*d*) Why does milk curdle on standing?

8. Give the name of (*a*) the sweetest sugar; (*b*) the cheapest; (*c*) the one most largely used.

9. What is the formula (*a*) of starch? (*b*) of cellulose? (*c*) What is the meaning of the letter x in these formulas?

10. Discuss starch as to (*a*) occurrence; (*b*) how obtained in pure state; (*c*) how to tell the source of any sample; (*d*) uses.

11. Discuss cellulose under the following heads: (*a*) occurrence; (*b*) how obtained in pure state; (*c*) uses.

12. Tell what is formed in each of the following cases:
- (*a*) Starch + boiling water
- (*b*) Starch + dilute hydrochloric acid
- (*c*) Sweet milk + rennet
- (*d*) Starch + heat (roasting)
- (*e*) Cellulose + concentrated hydrochloric acid
- (*f*) Cellulose + nitric acid (mixed with sulfuric acid)

13. Give the steps in the manufacture of each of the following: (*a*) paper; (*b*) rayon; (*c*) cellophane.

14. Discuss cellulose nitrates under the following headings: (*a*) how made; (*b*) composition; (*c*) different names applied to them; (*d*) various uses.

15. (*a*) What is meant by the term *photosynthesis*? (*b*) Under what conditions does photosynthesis take place?

16. What seems to be the function of the starch in plants and grains?

17. Some countries claim to be making dextrose from sawdust. (*a*) Do you think this possible? (*b*) If so, write the equation for the reaction involved.

II. ALKALOIDS

Plants supply us with medicines as well as with food and clothing. The medicines we use to cure our ills come from many sources. Most of them are made by chemists in their laboratories. Others come from animals, and still others from plants of various kinds. Prominent among those from plants is the class of compounds called *alkaloids*, because they have the properties of alkalies (bases), forming salts with acids. Most of them have strong physiological action.

Both the coffee bean and tea leaves contain the alkaloid *caffeine*; and whenever we drink a cup of tea or coffee, we are drinking a solution of caffeine (along with other compounds). Caffeine (or a derivative of it) is a common constituent of many headache medicines. Other alkaloids important in medicine are *quinine* (Fig. 357), used to cure malaria; *morphine*, which deadens pain; *strychnine*; and *cocaine*. All of these are white solids containing carbon, hydrogen, oxygen, and nitrogen. They are quite complex; quinine, for example, has the formula $C_{20}H_{24}N_2O_2$. *Nicotine*, ($C_{10}H_{14}N_2$), the active constituent of tobacco, is one of the few liquid alkaloids. It is used as an insecticide.

The alkaloids, as a rule, are very active, and most of them are intensely poisonous. Some of them, such as cocaine and morphine, are not only poisonous but very dangerous habit-forming drugs. *They should never be taken except under the direction of an expert physician.*

FIG. 357. Natives of Java cutting bark from certain trees. This bark contains quinine and is the source of this alkaloid

Quinine has recently (1944) been made in the laboratory but the method is too costly to be practical

III. THE ALCOHOLS

What is an alcohol? Just as there are many sugars, so there are many alcohols. Common alcohol — the one in all alcoholic liquors, such as wine and whisky — has the formula C_2H_5OH, and its chemical name is *ethyl alcohol* or *ethanol.* We may think of the alcohols as close relatives of the hydrocarbons. We may, then, define an alcohol as *a compound derived from a hydrocarbon by replacing one or more hydrogen atoms of the hydrocarbon with OH groups*, thus:

PARENT HYDROCARBON	DERIVED ALCOHOL
CH_4, methane	CH_3OH, methyl alcohol, methanol
C_2H_6, ethane	C_2H_5OH, ethyl alcohol, ethanol
C_3H_8, propane	C_3H_7OH, propyl alcohol, propanol

It will be noticed that the name of the alcohol is derived from that of the parent hydrocarbon. Some alcohols have common names as well.

Methyl alcohol, or methanol (CH_3OH) — a useful, although dangerous poison. This alcohol is also called *wood alcohol*, because it is formed when hard woods, such as beech, are heated in the absence of air. Formerly our supply came entirely from this source, but in more recent years chemists have found a cheaper way of making it. This is by heating carbon monoxide and hydrogen under suitable conditions. Most of the methyl alcohol now sold on the market is made in this way:

$$CO + 2\ H_2 \longrightarrow CH_3OH$$

Methyl alcohol is a colorless liquid boiling at 64.5°. When set on fire, it burns with an almost colorless flame. Since it is a good solvent for many organic compounds, it has a wide use for this purpose. It is poisonous, and many deaths have resulted from drinking methyl alcohol (mistaking it for common alcohol) or inhaling its vapor. It acts on the optic nerve and often causes permanent blindness when inhaled or taken in less than fatal doses.

When a mixture of the vapor of methyl alcohol and air is passed over hot copper (as a catalyst), a gaseous compound called *formaldehyde* (CH_2O) is produced:

$$2\ CH_3OH + O_2 \longrightarrow 2\ CH_2O + 2\ H_2O$$

A 40 per cent solution of this gas in water is sold by druggists under the name *formalin.* It is an important disinfectant and preservative.

Ethyl alcohol, or ethanol (C_2H_5OH) — ordinary alcohol. This is the alcohol present in all alcoholic liquors. It is a colorless liquid and, like methyl alcohol, is a good solvent for many organic compounds. It boils at 78.5° and, when set on fire, burns with a very hot and almost colorless flame:

$$C_2H_5OH + 3\ O_2 \longrightarrow 2\ CO_2 + 3\ H_2O$$

If taken in any considerable amounts, ethyl alcohol causes intoxication. In larger amounts it acts as a poison. The ordinary alcohol of the druggist contains about 95 per cent alcohol and 5 per cent water (by volume). Alcohol that does not contain more than 1 per cent of water is known as *absolute alcohol.* A 70 per cent solution of alcohol is a powerful antiseptic dressing in surgery.

When alcohol is heated with sulfuric acid, a low-boiling, colorless, inflammable liquid called *ethyl ether* is formed:

$$\underset{\text{ethyl alcohol}}{2\ C_2H_5OH} \longrightarrow \underset{\text{ethyl ether}}{(C_2H_5)_2O} + H_2O$$

This is one of the anesthetics most widely used in surgical operations, and was one of the first to be used in this way.

How ethyl alcohol is made. Alcohol is made by the action of baker's yeast upon solutions of various sugars such as dextrose:

$$C_6H_{12}O_6 \longrightarrow 2\ C_2H_5OH + 2\ CO_2 \uparrow$$

This action of yeast upon a sugar, changing it into alcohol and carbon dioxide, is called *alcoholic fermentation.* Yeast is a very simple form of plant life (Fig. 358) and grows in suitable sugar solutions. As the yeast plant grows it produces a substance called *zymase*, and it is this zymase that acts upon the sugar, changing it into alcohol and carbon dioxide.

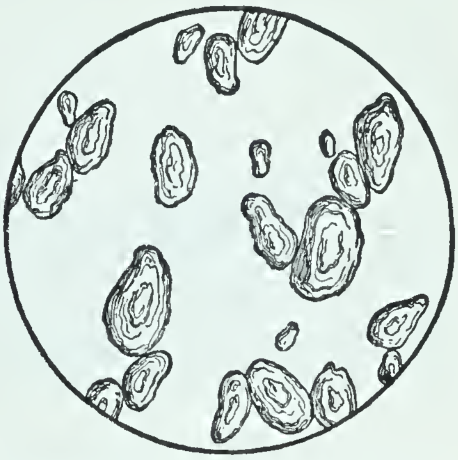


Fig. 358. Some cells of the yeast plant (magnified)

Most of the alcohol of commerce used in the United States is made by the fermentation of the sucrose of crude molasses shipped from Cuba (Fig. 359). A limited amount is also made from starch in the following way:

The starch is first mixed with water and malt (Fig. 360). Malt consists of barley grains that have been kept in a moist, warm place until the grains have sprouted. They are then heated until the small sprouts are killed. During the sprouting of the grain a small percentage of a substance known as *diastase* is formed, which acts on the starch, changing it into a sugar called *maltose.* Yeast acts on the maltose just as on dextrose, forming alcohol and carbon dioxide.

$$\text{Starch} \xrightarrow[\text{(diastase)}]{\text{malt}} \text{maltose} \xrightarrow[\text{(zymase)}]{\text{yeast}} \text{alcohol} + \text{carbon dioxide}$$

Ethyl alcohol can also be made by a synthetic process, starting with simple hydrocarbons. It is quite possible that the alcohol of the future will be made in this way, saving the sugars and starch for food.

Enzymes, a group of important catalysts. Attention has been called to the action of zymase, produced by the yeast plant, and of diastase, formed in the sprouting of barley. These belong to a class of substances known as *enzymes.* We

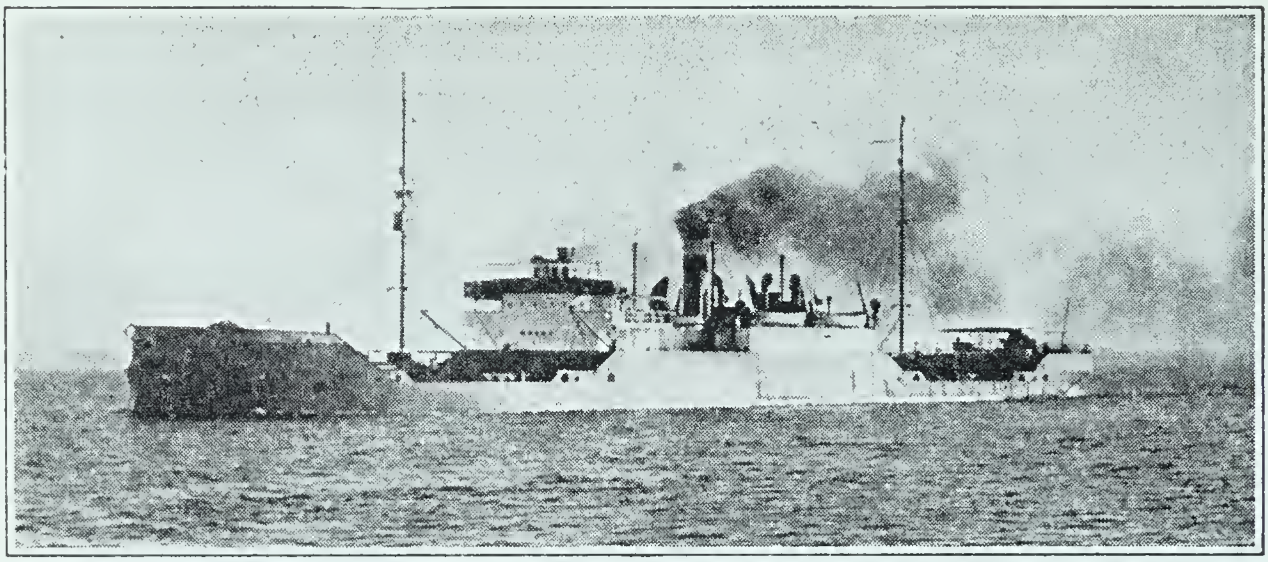


Fig. 359. A tank boat shipping crude molasses from Cuba to the United States to be used for making ethyl alcohol

Courtesy of the United States Industrial Alcohol Company

may define enzymes as *substances that are formed in living organisms and that act as catalysts in bringing about certain chemical changes.* Enzymes are remarkable specialists, each kind causing its own particular change. They are of great importance in the complex changes within our bodies.

Alcohol is both friend and foe. From very ancient times men of all nations have prepared alcoholic liquors of various kinds as beverages. Their alcoholic content is from 3 to 6 per cent in beers, 5 to 20 per cent in wines, and about 50 per cent in whisky and brandy. In order to discourage the excessive use of these beverages, as well as for revenue, governments have put heavy taxes on all kinds of alcoholic liquors. Pure alcohol is taxed as well, because imitation beverages are so easily made from it.

Fig. 360. Malt for preparing maltose

But alcohol has important scientific and industrial uses for which no good substitute has been found, and the government has no desire to interfere with these uses by heavy taxation. Accordingly, educational and scientific institutions can get alcohol for experimental purposes tax-free, while for industrial purposes the government allows the use of tax-free *denatured alcohol.*

Denatured alcohol. This liquid is alcohol to which has been added a definite amount of some substance that makes it unfit for use as a beverage but does not spoil it for manufacturing purposes. Such added substances are called *denaturants* and are strictly listed by the Federal government. Among these are methyl alcohol and certain petroleum products.

In the United States we use large quantities of alcohol in making a wide variety of commercial products such as lacquers, varnishes, toilet preparations, drugs, and dyes, as well as for an antifreeze used in automobile radiators in winter. In some foreign countries where petroleum supplies are limited, a mixture of alcohol and gasoline is used as a fuel for running automobiles. An effort is being made to use a similar mixture in the United States, not only to save our waning petroleum supplies but also to help the farmer by creating a market for starch (from corn and potatoes), from which the alcohol can be made. Such a use would probably lead to the synthetic manufacture of the compound unless this were prohibited by law.

Ethylene glycol ($C_2H_4(OH)_2$): an alcohol with two OH groups in each molecule. We have seen that if we replace one atom of hydrogen in ethane (C_2H_6) by an OH group, we get ethyl alcohol, C_2H_5OH. If we replace *two* atoms by *two* OH groups, we get the alcohol $C_2H_4(OH)_2$, called *ethylene glycol* or simply *glycol.* This is a colorless liquid of high boiling point (197.5°) and is the compound sold under the trade name of *Prestone* as an antifreeze in automobile radiators.

Glycerol ($C_3H_5(OH)_3$); an alcohol with three OH groups in each molecule. We are not likely to think of glycerol (common glycerin) as an alcohol. Yet it is derived from the hydrocarbon propane, C_3H_8 (p. 429), by replacing three atoms of hydrogen with three OH groups; and so, according to our definition (p. 469), it is a true alcohol. This sweet sirupy liquid is a by-product in the manufacture of soap, as we shall see later on.

Glycerol is a perfectly safe, nonpoisonous, harmless compound; but nitric acid changes it into one of our most dangerous and powerful explosives, $C_3H_5(NO_3)_3$, commonly called *nitroglycerin* — a remarkable change in properties:

$$C_3H_5(OH)_3 + 3\ HNO_3 \longrightarrow C_3H_5(NO_3)_3 + 3\ H_2O$$

Nitroglycerin is explosive because it is very unstable and, when it decomposes, yields a large volume of gases, chiefly carbon dioxide, nitrogen, and oxygen. One volume of the liquid gives about 1300 volumes of these gases, which expand by the heat of the reaction to more than 10,000 volumes. This explains the great force of the explosion (Fig. 361). Dynamite (Fig. 362) consists of nitroglycerin soaked up in wood pulp, together with some oxidizing agent such as ammonium nitrate. It is not so easily exploded as pure nitroglycerin and can be shipped with safety.

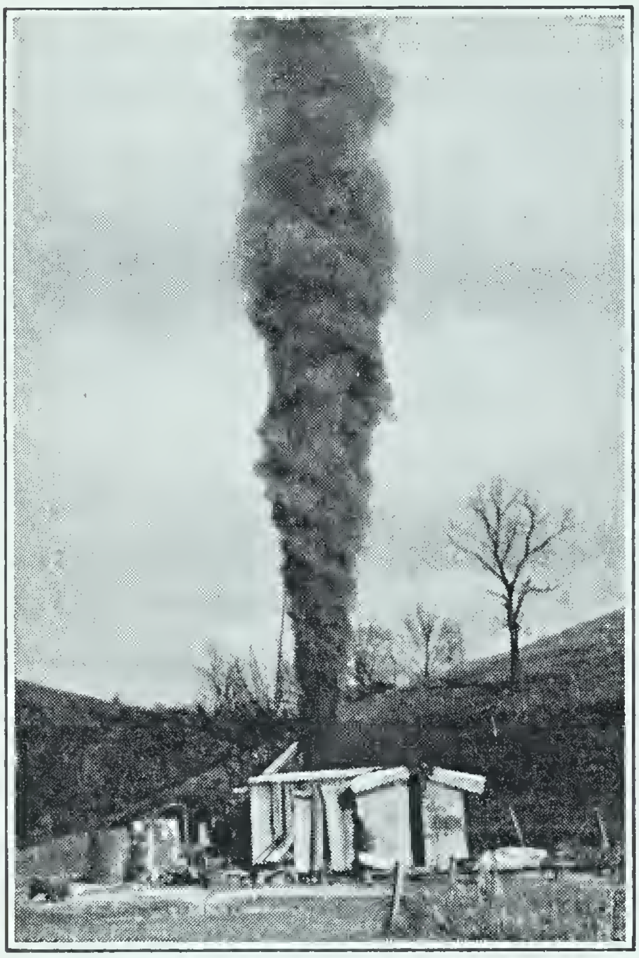


FIG. 361. "Shooting" an oil well

When a gas (or oil) well is drilled, a charge of nitroglycerin is often lowered to the bottom of the well and exploded. The force of the explosion tears the ground open so that the gas may escape from the surrounding earth into the well. The picture shows the "shooting" of such a well

Chemical changes in breadmaking. It may come as a surprise to learn that one of the chief reactions that take place in breadmaking is the changing of sugar into alcohol and carbon dioxide — the same change that takes place in the manufacture of alcohol and alcoholic liquors. Yet such is the case. Of course there are many kinds of bread, but we shall consider only the ordinary bread made from white flour. The average composition of this flour is as follows:

Water	11.9%
Nitrogenous matter, chiefly gluten	13.3%
Fats	1.5%
Starch	72.7%
Mineral matter	0.6%

In making bread the flour is mixed with water, milk, yeast, and a little sugar and salt, and the resulting dough is set aside in a warm place for a few hours. The zymase from the yeast (p. 471) causes the added sugar, as well as some formed from the starch, to undergo alcoholic fermentation. The resulting carbon dioxide pushes its way upward through the dough. The yeast plant thrives best at about 30°; so the dough is put in a warm place. In the process of baking, the heat drives off the alcohol and also expands the bubbles of carbon dioxide caught in the dough. This causes the dough to become porous and makes the bread light.

Fig. 362. A stick of dynamite with fuse attached

How foods may be kept from spoiling. We have seen that such changes as the souring of milk and the fermentation of sugar are due to the presence of minute organisms. Many other changes, such as *decay*, are due to the same cause. Since the spores or seeds of these organisms are present in the air, they easily get into foods and start the changes, so that it is difficult to keep many kinds of foods from spoiling.

Some of the ways of doing this are the following: (1) The food may be kept in a cold place so that the growth of the organism is stopped or at least slowed up by the low temperature (cold storage). (2) The food may be heated until all the organisms in it are killed, and then sealed in airtight containers. Canned vegetables are kept sweet in this way. Any food heated so as to destroy the organisms in it is said to be *sterilized*. (3) We may dry the food so that the organisms have not the moisture necessary for growth. (4) We may add so much of some food material, such as salt or sugar, that the medium is too concentrated for the organism to grow in it. In this way our common jellies are preserved by the addition of large percentages of sugar. (5) Finally, we may add a *preservative*, a small percentage of which will prevent the growth of the organisms.

Of course, we must be on our guard against using any food preservative that might be injurious to health. Many experiments have been made to find a safe and reliable preservative. At present it is legal to use the compound called *sodium benzoate*, but only under certain restrictions, one of which is that the percentage present must be printed on the label. As a general rule it may be said that to keep foods from spoiling, cleanliness and sterilization are better than an added preservative.

SUMMARY OF PARTS II AND III IN QUESTION FORM

1. (*a*) What name is given to a group of basic compounds found in plants? (*b*) What are the general properties of these compounds? (*c*) Mention one use of many of these compounds.

2. (*a*) To what group of compounds are the alcohols related? (*b*) Define the term *alcohol* and give two examples to illustrate your definition.

3. Discuss methyl alcohol under the following headings: (*a*) names; (*b*) methods of making; (*c*) properties; (*d*) products of oxidation; (*e*) uses.

4. (*a*) What is yeast? (*b*) What change takes place when yeast is added to dextrose?

5. Write a paragraph about the production of ethyl alcohol, including the following words: (*a*) barley; (*b*) malt; (*c*) diastase; (*d*) maltose; (*e*) sugar; (*f*) yeast; (*g*) starch; (*h*) fermentation.

6. Distinguish between (*a*) denatured alcohol, (*b*) absolute alcohol, and (*c*) the ordinary alcohol sold by the druggist.

7. Write the equation for the reaction that takes place when ethyl alcohol is burned.

8. (*a*) What are the uses of alcohol? (*b*) Why is it taxed?

9. (*a*) Show that glycerol is an alcohol. (*b*) Distinguish between glycerol, nitroglycerin, and dynamite.

10. (*a*) What name is given to the catalysts secreted by certain living organisms? (*b*) Give two examples to illustrate.

11. Give the chief changes that take place in breadmaking.

12. (*a*) What causes food to spoil? (*b*) Mention four ways of preventing foods from spoiling.

IV. SOME ORGANIC ACIDS AND THEIR DERIVATIVES

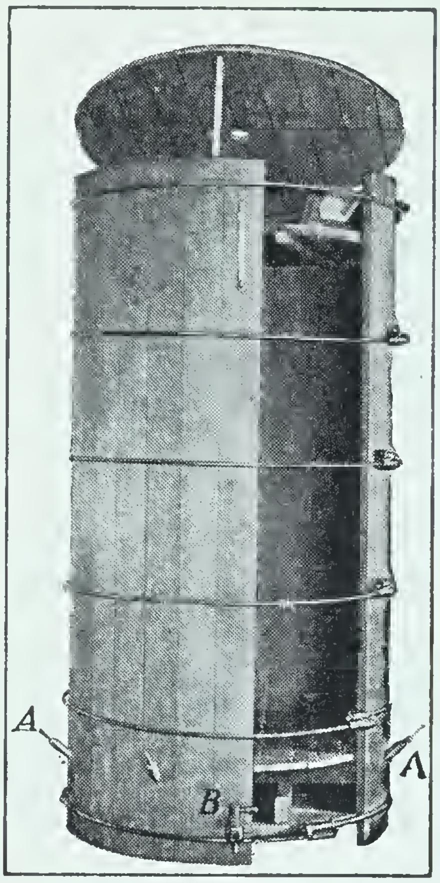
Many foods contain acids. The sour taste of many foods tells us of the presence of acids. Vinegar contains *acetic acid*; lemons and grapefruit, *citric acid*; and sour milk, *lactic acid.* Like all organic compounds, these acids contain carbon, and they belong to a general group of compounds called the *organic acids.* We shall now study a few of the most important of these.

Acetic acid, the acid of vinegar ($C_2H_4O_2$, or $H \cdot C_2H_3O_2$). While there are four atoms of hydrogen in each molecule of this acid, only one of these can be replaced by a metal to form a salt. In other words, acetic acid is *monobasic* (p. 243). We indicate this fact in the formula by separating the replaceable hydrogen from the rest of the molecule, thus: $H \cdot C_2H_3O_2$.

Acetic acid has long been made by the destructive distillation of wood (p. 141). In recent years, however, chemists have invented a process starting with the hydrocarbon acetylene, and this method is rapidly replacing the older one. The pure acid is a colorless liquid and has a strong, pungent odor. Some of its salts (the acetates) are well-known compounds. For example, lead acetate is the white solid called *sugar of lead.*

The composition of vinegar. The grocer has for sale a number of different kinds of vinegar, such as cider vinegar, wine or grape vinegar, malt vinegar. Each of these is named from the raw material used in making it. They all must contain not less than 4 g of acetic acid in 100 ml of the liquid, a requirement fixed by a Federal statute. In addition to the acid, each one contains small percentages of substances derived from the raw materials used in its manufacture. The chemist is able to tell the source of any sample of vinegar by evaporating it and examining the nature of the solids left.

The chemical changes involved in making vinegar. It has long been known that cider left so that air has access to it will slowly turn into vinegar. Two chemical changes take place in the process: (1) The sugar in the cider first under-



The generator is filled loosely with beech shavings. Vinegar is first sprayed into the top of the cask in order to introduce the essential organism. This organism attaches itself to the shavings, which are used because they present a large surface. Next, a dilute solution of alcohol (hard cider, in the case of cider vinegar) is sprayed into the top of the cask while air is admitted at the bottom, *A*, *A*. In this way the alcohol and oxygen are brought into intimate contact, and the oxidation takes place rapidly as the liquid trickles down over the shavings. The resulting vinegar is drawn off at the bottom, *B*, of the cask

FIG. 363. A generator for the manufacture of vinegar

goes alcoholic fermentation, forming *hard cider*, which contains from 4 to 8 per cent of alcohol, the percentage depending upon the amount of sugar in the cider. (2) The alcohol is then oxidized to acetic acid by the oxygen in the air, through the agency of a microscopic plant, spores of which are everywhere in the air:

$$C_2H_5OH + O_2 \longrightarrow H \cdot C_2H_3O_2 + H_2O$$

The oxidation of alcohol into acetic acid in this way is known as *acetic fermentation.* Small percentages of other compounds are also formed in this process, and these give vinegar its distinctive odor.

Instead of starting with cider in making vinegar one may use almost any substance that contains starch or sugar, these compounds first being changed into alcohol as explained in connection with the manufacture of alcohol. The cheapest vinegar, *distilled vinegar*, is made from dilute alcohol.

The older way of making vinegar was simply to store cider in barrels until the fermentation was complete, a process taking several weeks. In the modern method the change is completed in a few hours, as explained in Fig. 363.

Some common fruit acids. Most fruits contain at least a small percentage of acids. Among these are the following: (1) Malic acid ($H_2 \cdot C_4H_4O_5$) is present in apples and pears. It is a dibasic acid (p. 243), as the formula shows. (2) Citric acid ($H_3 \cdot C_6H_5O_7$) occurs in lemons and grapefruit. (3) Tartaric acid ($H_2 \cdot C_4H_4O_6$) occurs in many fruits, usually in the form of its salts. Its potassium acid salt, $KH \cdot C_4H_4O_6$, is a white solid called *cream of tartar.* This is present in grape juice, from which it is separated. It is used in making baking powders. The free acid is used in making "pop" and other soft drinks.

Palmitic acid, stearic acid, oleic acid — three acids we get from oils and fats. These acids are of great importance to us because their derivatives are the chief part of many of the fats and oils present in our foods. All three are monobasic, as the following formulas show:

Palmitic acid ($H \cdot C_{16}H_{31}O_2$)	a white solid melting at 64°
Stearic acid ($H \cdot C_{18}H_{35}O_2$)	a white solid melting at 69°
Oleic acid ($H \cdot C_{18}H_{33}O_2$)	a colorless, oily liquid

V. ESTERS: THE CHIEF CONSTITUENTS OF FATS AND OILS

What is an ester? Just as each molecule of an acid contains one or more hydrogen atoms that can be replaced by metals to form salts, so this same hydrogen of the acid can be replaced by hydrocarbon radicals, such as CH_3 (methyl), C_2H_5 (ethyl), to form compounds known as *esters.* And, just as salts can be prepared by the action of acids on *bases,* so esters can be prepared by the action of acids on *alcohols.*

$$\underset{\text{acetic acid}}{H \cdot C_2H_3O_2} + \underset{\text{ethyl alcohol}}{C_2H_5OH} \longrightarrow \underset{\substack{\text{ethyl acetate} \\ \text{(an ester)}}}{C_2H_5 \cdot C_2H_3O_2} + HOH$$

An ester is a compound formed by replacing the hydrogen of an acid by a hydrocarbon radical.

The esters form a very important group of compounds. Many have a pleasant odor, and the fragrance of flowers is often due to them. They are common constituents of perfumery and flavoring extracts. Some of them are valuable foods and necessary to our health.

Something about oils and fats. We have already learned about certain oils, such as coal oil (kerosene), lubricating oils, and fuel oils. We get all these from petroleum, and they are made up of hydrocarbons. But we have another very large and important group of oils and fats that we get from animal and vegetable sources, and these have an entirely different composition from that of the petroleum oils. Indeed, the seeds and fruits of most plants, as well as many of the tissues of animals, contain oils that can be got by pressure or by some suitable solvent. For example, we have olive oil, corn oil, coconut oil, cod-liver oil, cottonseed oil, and a host of others. Many of these are excellent foods, while others are the raw materials used in making such valuable things as soap and glycerol.

The composition of the animal and vegetable oils and fats. The oils and fats from animal and vegetable sources are composed chiefly of three esters called *palmitin*, *stearin*, and *olein*. These esters are derived from palmitic, stearic, and oleic acids by replacing the hydrogen of the acids by the hydrocarbon radical C_3H_5. This is called *glyceryl*, because it is present in glycerol ($C_3H_5(OH)_3$). This radical has a valence of 3, and so replaces three atoms of hydrogen. But each molecule of palmitic, stearic, and oleic acids has only one replaceable hydrogen atom. So it follows that three molecules of an acid are required to make one molecule of the ester of that acid. These relations are shown as follows:

$H \cdot C_{16}H_{31}O_2$ (palmitic acid)	$C_3H_5(C_{16}H_{31}O_2)_3$ (palmitin)
$H \cdot C_{18}H_{35}O_2$ (stearic acid)	$C_3H_5(C_{18}H_{35}O_2)_3$ (stearin)
$H \cdot C_{18}H_{33}O_2$ (oleic acid)	$C_3H_5(C_{18}H_{33}O_2)_3$ (olein)

The names *palmitin*, *stearin*, and *olein* are really common names. The chemical names for these esters are *glyceryl palmitate*, *glyceryl stearate*, and *glyceryl oleate*.

Palmitin and stearin are white solids, and make up the bulk of the solid fats. Olein is a liquid and makes up a large percentage of the oils, such as olive oil, and of lard (Fig. 364).

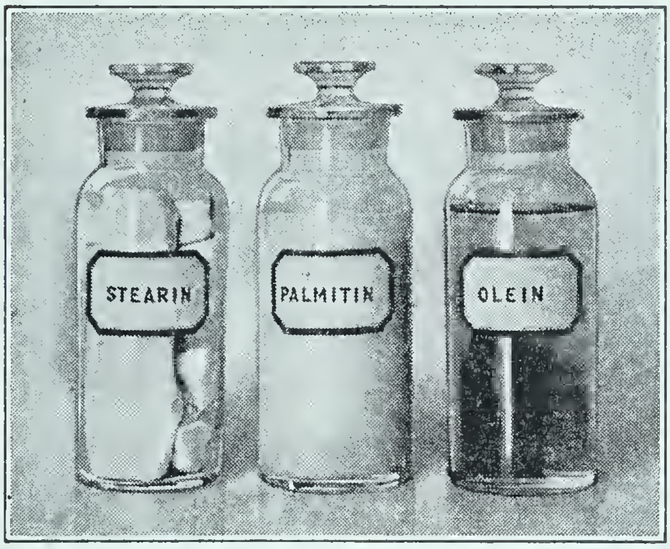


FIG. 364. The three chief constituents of oils and fats

The refining of vegetable oils. In separating oils from their source material there are sure to be some other substances dissolved in the oil. Sometimes these substances add to the flavor of the oil, as is the case with olive oil. More often they spoil its looks and taste. For example, crude cottonseed oil (Fig. 365) and corn oil are black and not edible. It is possible to remove these impurities, and the oils when so refined are very much alike in composition. Refined corn oil and cottonseed oil (Fig. 365) are now largely used as salad oils in place of the more expensive olive oil, and only an expert can distinguish between them. These oils have many uses (Fig. 12).

The difference between butter and oleomargarine. A Federal law requires that butter must contain not less than 80 per cent of fat from milk. This fat, like other fats and oils, consists primarily of palmitin, stearin, and olein, but its butter flavor is due to the presence of small percentages of other fats found in milk. Oleomargarine differs from butter mainly in the fact that a smaller percentage of the fats characteristic of butter is present. It is made from fats obtained from cattle and hogs. Many times vegetable oils, such as coconut oil and cottonseed oil, are used. These fats are churned with milk or mixed with a small quantity of butter, in order to add a little of the fat to give the flavor of butter.

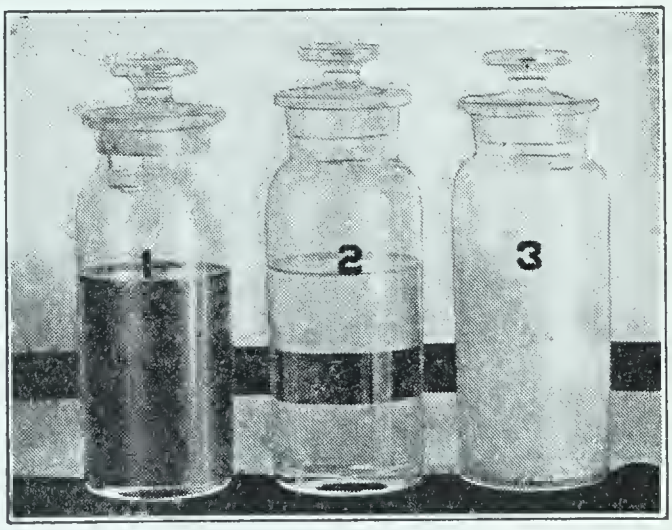


FIG. 365. Cottonseed oil

In jar 1 is the crude cottonseed oil as pressed from the seed; in jar 2 is the refined oil; and in jar 3 the oil after hydrogenation

While it is a common practice to color butter, the Federal laws permit the coloring of oleomargarine only upon the payment of a tax of 10 cents for each pound colored. Some of the states forbid the sale of colored oleomargarine under any conditions.

Hydrogen changes oils into solid fats; the hydrogenation of oils. If the formulas of stearin and olein are compared, it will be seen that the former differs from the latter in that it contains six more atoms of hydrogen in each molecule. Now when hydrogen is brought in contact with olein under the proper conditions and in the presence of a suitable catalyst (finely divided nickel), the olein takes up the additional hydrogen and becomes solid stearin. It is possible in this way to change the oils into solid fats (Fig. 365). Certain commercial fats used in cooking, mostly sold under trade names (such as Crisco), are made by this process from the comparatively inexpensive cottonseed oil. They are valuable foods, and for certain purposes are preferable to lard.

VI. SOAPS

What soaps are composed of, and how they are made. Someone has said, "Tell me the amount of soap used per thousand inhabitants of a nation, and I will tell you how far advanced in civilization that nation is." Whether or not this claim could be made good, it is certain that soap is a large factor in the welfare of all civilized people.

To make soap we have only to heat a fat or oil with a solution of sodium hydroxide. By this means the palmitin, stearin, and olein present in the fat are changed into glycerol and the sodium salts of palmitic, stearic, and oleic acids. A mixture of these three sodium salts (sodium palmitate, sodium stearate, and sodium oleate) makes up the bulk of all ordinary soaps. With stearin the reaction runs as follows:

$$\underset{\text{stearin}}{C_3H_5(C_{18}H_{35}O_2)_3} + \underset{\substack{\text{sodium}\\\text{hydroxide}}}{3\,NaOH} \longrightarrow \underset{\text{glycerol}}{C_3H_5(OH)_3} + \underset{\text{sodium stearate}}{3\,NaC_{18}H_{35}O_2}$$

When the reaction between the fat and sodium hydroxide is complete, the soap is in the form of a colloidal dispersion in water. The soap is then coagulated by the addition of salt (p. 415). The watery liquid contains the glycerol formed in making the soap (see the equation above). This is the source of nearly all our glycerol, so that every soap factory is a glycerol factory as well. Some of the steps in soap-making are shown in Fig. 367.

Potassium hydroxide may be used in place of sodium hydroxide in making soap, but the product is a "soft soap" and not so suitable for molding into cakes.

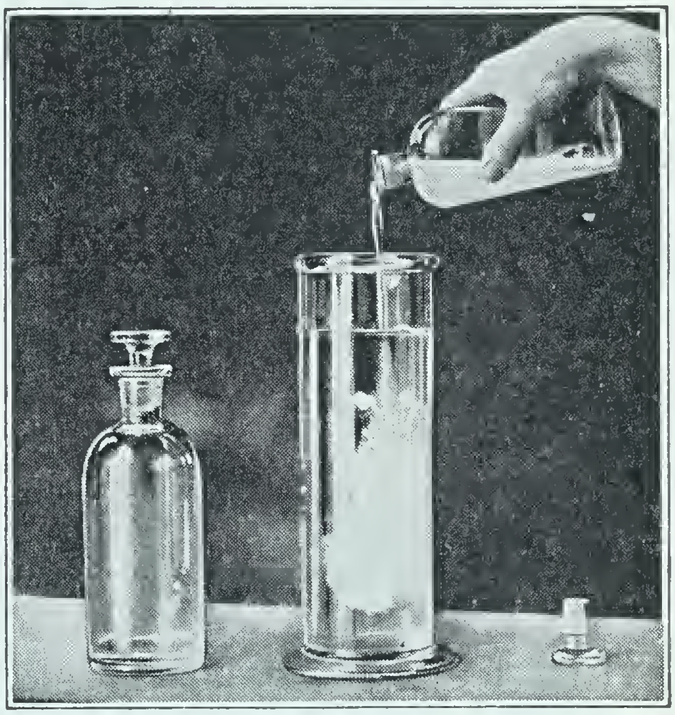


FIG. 366. Explaining the action of hard water on soap

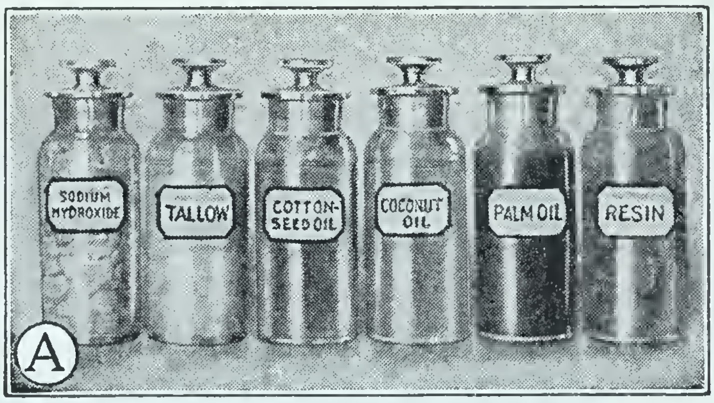
When a solution of a calcium (or magnesium) salt is added to a soap dispersion, a white precipitate of calcium stearate forms

There are many kinds of soap. While all the ordinary soaps are made in the same way, we are familiar with many different kinds. The difference between these is due partly to the different oils and fats used, and partly to certain foreign substances added to the soap during its manufacture. For example, floating soaps owe their lightness to bubbles of air. Naphtha soaps contain a small percentage of naphtha. Scouring soaps contain finely powdered silica or volcanic ash. Sometimes sodium carbonate or borax is added to the soap. Various perfumes and different coloring matters may also be added.

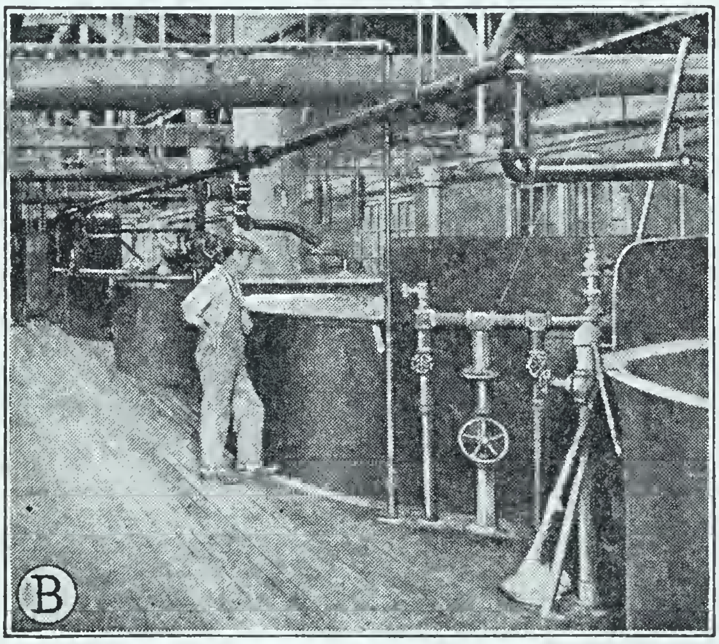
The properties of soap. When added to soft water, soap seems to dissolve. In reality, the soap forms with the water a colloidal dispersion (p. 410) which is slightly alkaline in reaction. If an acid, such as hydrochloric acid, is added to the colloidal dispersion, the insoluble organic acids are liberated from their salts and are precipitated:

$$\underset{\text{sodium stearate}}{NaC_{18}H_{35}O_2} + HCl \longrightarrow NaCl + \underset{\text{stearic acid}}{H \cdot C_{18}H_{35}O_2}\downarrow$$

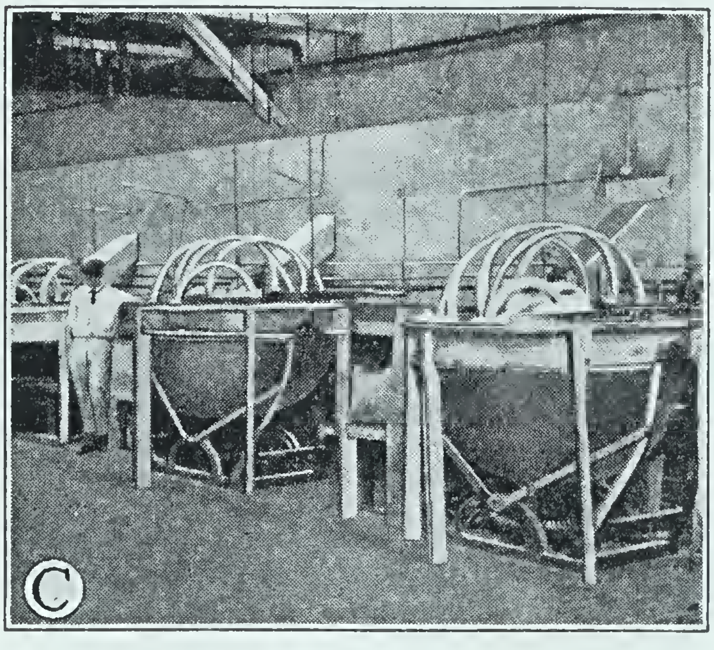
The calcium and magnesium salts of oleic, palmitic, and stearic acids are insoluble in water and are therefore precipi-



The essential materials are (1) an animal or vegetable fat or oil and (2) an alkali. The fats and oils used are tallow and cheap vegetable oils, such as cottonseed oil, palm oil, and coconut oil. The alkali used is sodium hydroxide. Resin may be used instead of fat

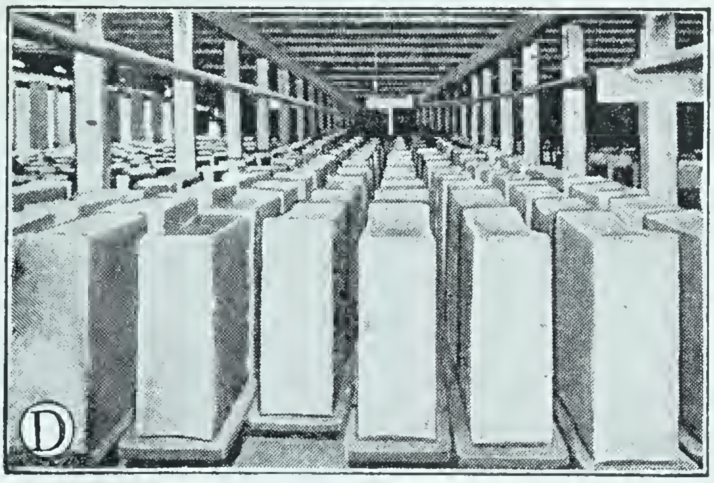


The melted fat or the oil is heated with a solution of sodium hydroxide in large iron kettles. These kettles are so large that 500,000 lb of soap, or even more, may be made at one time. The resulting soap forms a colloidal dispersion in the water present and is coagulated by adding sodium chloride — a process known as "salting out"

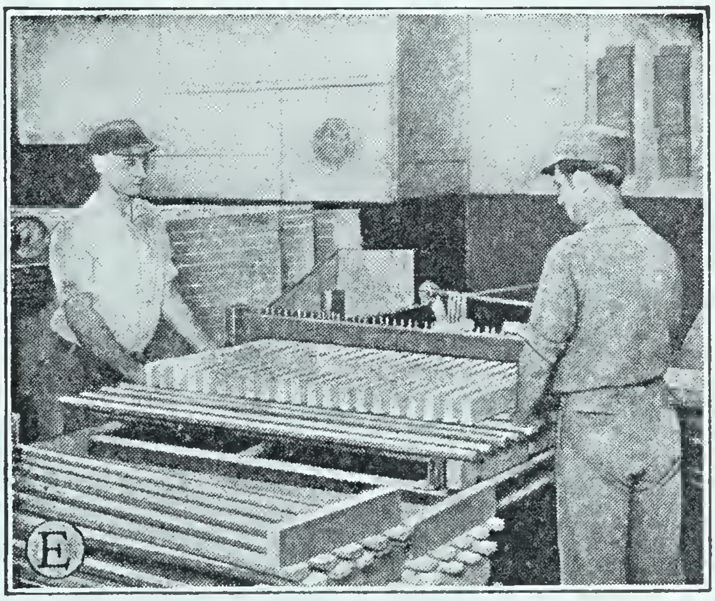


The coagulated soap is stringy or fibrous. To overcome this and also to make the soap uniform, it is pumped into large crutchers, or stirring bowls, and is then stirred until it is uniform. If it is desired to add other materials (p. 483), these are added and mixed with the soap in the crutchers

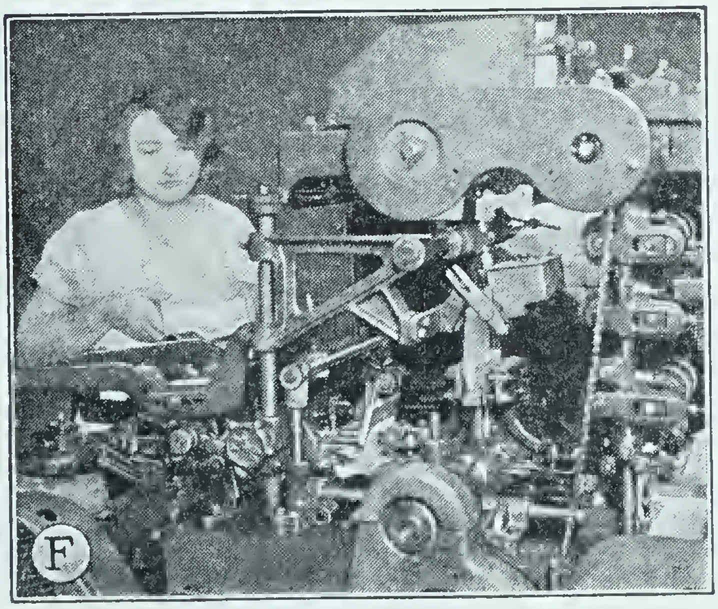
Fig. 367, A, B, C. Some steps in the manufacture of soap



The soap while still fluid is allowed to flow from the stirring bowls into large boxes, or frames, open at the top. When the soap has hardened, the sides of the boxes are removed, leaving large cakes of soap, as can be seen in D



The large cakes of soap shown in D are next cut by machinery, first into flat slabs, then into long bars, and finally into cakes of appropriate size, depending upon their quality and use



As the final step in its manufacture the soap is stamped and wrapped by means of special machinery, and is now ready for the market

Courtesy of Procter & Gamble

Fig. 367, D, E, F. Some steps in the manufacture of soap tated when a calcium or magnesium compound is added to a colloidal dispersion of soap (Fig. 366):

$$\underset{\text{sodium stearate}}{2\,NaC_{18}H_{35}O_2} + CaCl_2 \longrightarrow 2\,NaCl + \underset{\text{calcium stearate}}{Ca(C_{18}H_{35}O_2)_2}\downarrow$$

It is due to this fact that soaps do not lather with hard waters but form a curdy precipitate; for hard waters always contain calcium and magnesium salts in solution.

The cleansing action of soap is not thoroughly understood, but seems to be partly due to the fact that soap easily forms an emulsion (p. 417) with oils. When soap is rubbed on the skin, any oily substances present are emulsified and washed away. Adsorption also plays an important part.

VII. COAL-TAR COMPOUNDS

The source of coal tar. In studying coal gas (p. 440) we learned that when coal is heated in the absence of air not only is coal gas formed but also coke, ammonia, and a thick, black liquid called *coal tar*. In the early days of coal gas this tar was a great nuisance and expense to the makers of the gas; for they had to get rid of it in some way. Finally the chemists were called in, and they began a study of the tar to find out what it was composed of and to see whether some use could be found for it. The result was that the chemists got from this worse than useless tar thousands of compounds that are of great value to us in many ways.

The process of refining coal tar (that is, separating it into its constituents) is very much like the refining of petroleum (p. 430). The tar is heated in large iron stills, and the different products distill over in the general order of their boiling points.

What is the composition of coal tar? Coal tar is a mixture of various compounds, colored black by finely divided carbon. At least one hundred and twenty-five compounds have been found in coal tar, but most of these are in such small percentages that it pays to separate only a few of them — not more than twelve or fifteen. The six most important of these are shown in Fig. 368. Each of these compounds is the raw material for making other compounds, and these in turn for

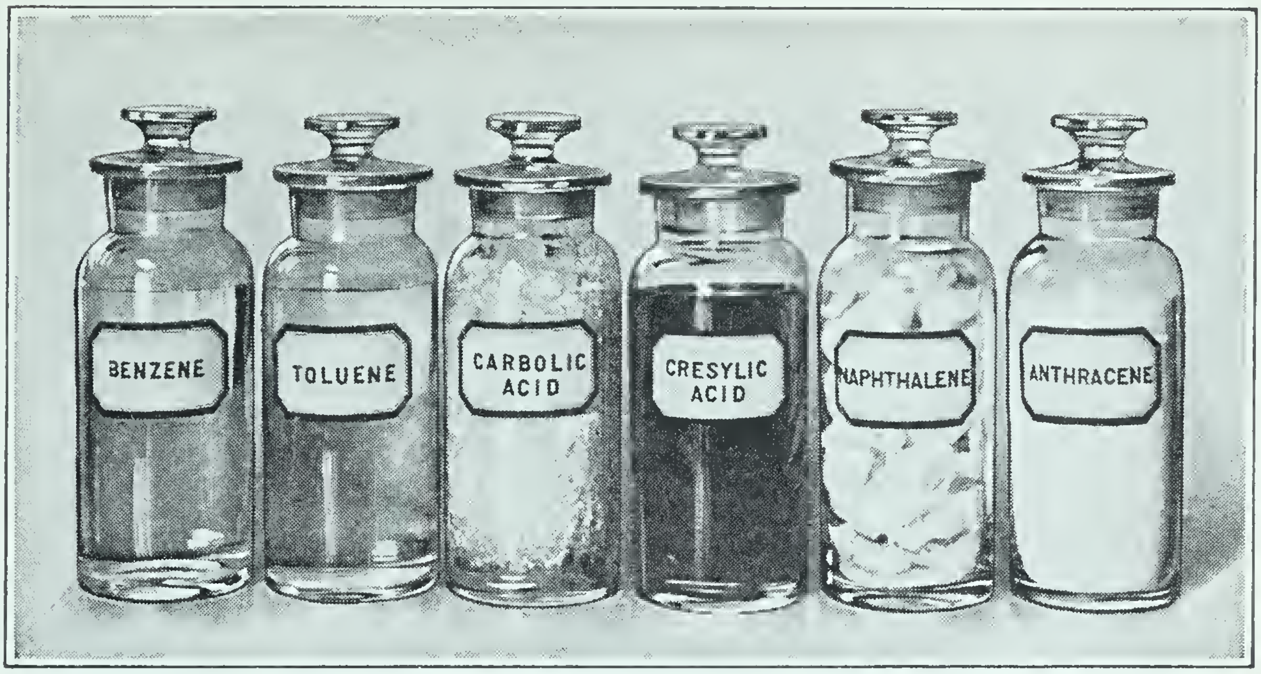


Fig. 368. The more important compounds obtained directly from coal tar by distillation

still others. *All these compounds, whether present in coal tar or made from those that are present, are called coal-tar compounds.* Many thousands of them have been made.

The chart (Fig. 369) gives us some idea of the kinds of compounds that we owe to coal tar, and also the relation of the compounds to each other.

The properties and uses of some important coal-tar compounds. We shall describe only six compounds (Fig. 368) obtained directly from coal tar, and a few typical compounds derived from each.

1. ***Benzene* (C_6H_6).** This is a colorless, very inflammable liquid boiling at 79.6°. When it is treated with nitric acid, *nitrobenzene* ($C_6H_5NO_2$) is formed, and, on reduction, this gives a nearly colorless liquid called *aniline* ($C_6H_5NH_2$). From this, in turn, hundreds of dyes of all colors are made.

2. ***Toluene* (C_7H_8).** This hydrocarbon looks and acts like benzene, but it has a higher boiling point. When treated with nitric acid, it forms the solid compound called *trinitrotoluene* (commonly called T.N.T.), so largely used as an explosive in the World War. From toluene it is easy to make benzoic acid, whose sodium salt, *sodium benzoate*, is a common food preservative (p. 476). Or we can make *saccharine*, a compound about five hundred times as sweet as sugar. Although so sweet, saccharine is not a food, and its use in food is prohibited by Federal statute.

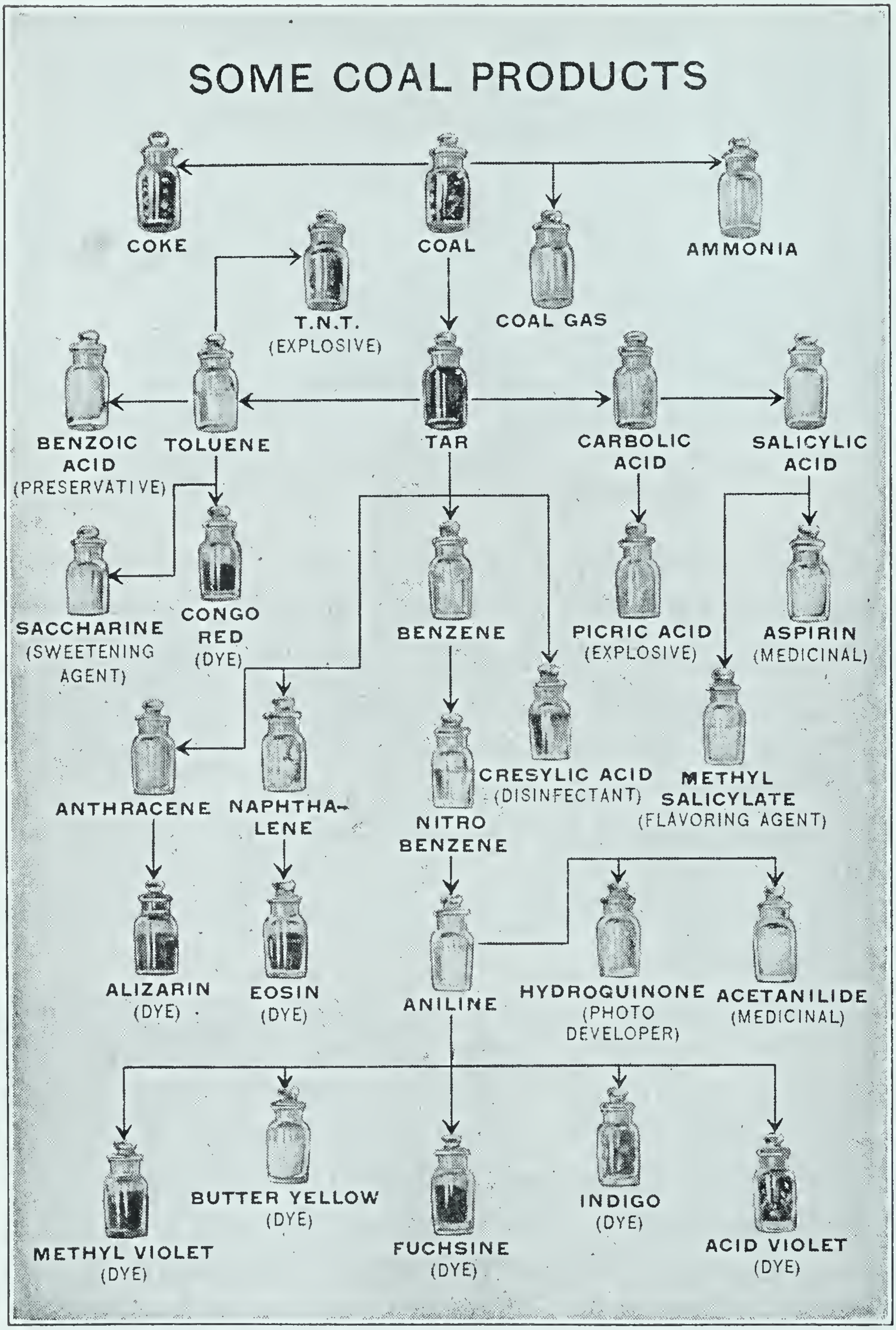

SOME COAL PRODUCTS
COKE
COAL
AMMONIA
COAL GAS
T.N.T.
(EXPLOSIVE)
BENZOIC
ACID
(PRESERVATIVE)
TOLUENE
TAR
CARBOLIC
ACID
SALICYLIC
ACID
SACCHARINE
(SWEETENING
AGENT)
CONGO
RED
(DYE)
BENZENE
PICRIC ACID
(EXPLOSIVE)
ASPIRIN
(MEDICINAL)
ANTHRACENE
NAPHTHALENE
NITRO
BENZENE
CRESYLIC ACID
(DISINFECTANT)
METHYL
SALICYLATE
(FLAVORING AGENT)
ALIZARIN
(DYE)
EOSIN
(DYE)
ANILINE
HYDROQUINONE
(PHOTO
DEVELOPER)
ACETANILIDE
(MEDICINAL)
METHYL VIOLET
(DYE)
BUTTER YELLOW
(DYE)
FUCHSINE
(DYE)
INDIGO
(DYE)
ACID VIOLET
(DYE)

FIG. 369. Chart showing the derivation of some coal-tar compounds

Following the arrows backward, we can trace the *ancestry* of each compound. Thus toluene is obtained directly from coal tar, as indicated by the arrow, while from toluene we prepare benzoic acid, trinitrotoluene (T.N.T.), saccharine, and Congo red

3. ***Carbolic acid (phenol) (C_6H_5OH).*** The pure acid is a white solid and is very poisonous. From it can be made *salicylic acid*, and from this the familiar medicine *aspirin*. Carbolic acid is also used in making *picric acid* (an explosive and medicine) and plastics (Fig. 307).

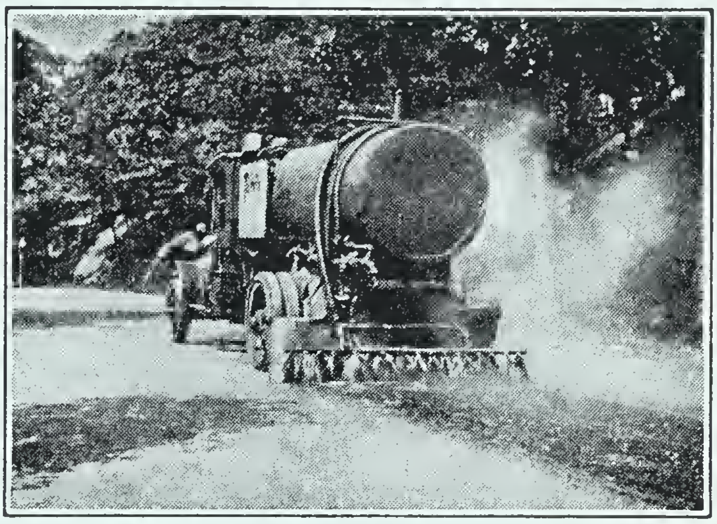


FIG. 370. Using pitch obtained from coal tar in road construction

4. ***Cresylic acid (cresol) (C_7H_7OH).*** This substance is the basis of nearly all the common disinfectants used in our homes for such purposes as cleaning drainpipes and sinks. It is also used for killing injurious insects that attack animals.

5. ***Naphthalene ($C_{10}H_8$).*** This is a white crystalline compound, best known to us in the form of *moth balls.*

6. ***Anthracene ($C_{14}H_{10}$).*** This is a nearly white solid from which is made *alizarin*, one of our most valuable dyes; it dyes cotton a brilliant red.

Coal-tar dyes — there are many thousands of them. The use of dyes is as old as history. Until the discovery of the aniline dyes in 1856, the dyes used were mostly got from plants or wood, although the one most highly prized by the ancients, the Tyrian purple, was obtained from a shellfish that lived in the Mediterranean. The discovery of the first aniline dye by Perkin (Fig. 16) soon led to the discovery of others, until now many thousands of these dyes, of every imaginable color, have been made, and new ones are added to the list almost daily. They have almost entirely replaced dyes from other sources. Indeed, the two most common of the vegetable dyes, *indigo* and *alizarin*, are now manufactured at lower cost from coal-tar compounds, while the Tyrian purple, which was formerly worth more than its weight in gold, is now easily made from indigo.

Most of the aniline dyes have a very complex composition. For example, the formula of indigo is $C_{16}H_{10}N_2O_2$.

Pitch is also made from coal tar. When coal tar is distilled, there remains in the still a thick, tarry mass called *pitch.* This is used in building roads, especially as a binder to hold together the sand and crushed stone which make the solid part of the roadway (Fig. 370).

SUMMARY OF PARTS IV, V, VI, AND VII IN QUESTION FORM

1. Name and give the formula of an organic acid that is (*a*) a liquid present in vinegar; (*b*) a white crystalline solid, an acid salt of which occurs in grapes; (*c*) a white solid, a derivative of which occurs in fats.

2. Give the chemical changes that take place in making vinegar (*a*) from dilute alcohol; (*b*) from cider; (*c*) from starch.

3. What are the changes that take place (*a*) in alcoholic fermentation? (*b*) in acetic fermentation? (*c*) What is the cause of each of these changes?

4. (*a*) How could you hasten the speed of the reactions that take place in making vinegar from cider? (*b*) How could you retard them?

5. Give the name of the class of compounds formed by replacing the hydrogen of an acid by (*a*) a metal; (*b*) a hydrocarbon radical.

6. What elements are present in the oils obtained (*a*) from petroleum? (*b*) from animal and vegetable sources?

7. Prepare a table under the following heads, giving information in regard to the three principal acids whose derivatives are present in oils and fats.

NAME	FORMULA	NAME OF ESTER PRESENT IN FATS	FORMULA OF ESTER PRESENT IN FATS

8. State clearly the difference (*a*) between the composition of butter and oleomargarine; (*b*) between olive oil and cottonseed oil.

9. (*a*) How can olein be changed into stearin? (*b*) What is the process called?

10. Discuss soap under the following heads: (*a*) materials used; (*b*) process of making; (*c*) compounds formed; (*d*) how the soap is separated in solid form.

11. Write the equations for the reactions that take place when a colloidal dispersion of soap is treated with each of the following reagents: (*a*) sodium chloride; (*b*) hydrochloric acid; (*c*) calcium chloride.

12. Inspect Fig. 369, and select four substances that are directly formed by heating soft coal in closed retorts.

13. What name is given to the process referred to in question 12?

14. Define the term *coal-tar compound.*

15. Inspect Fig. 369, and select a compound obtained from coal tar which serves for the preparation of all four of the following: a dye; a preservative; an explosive; a sweetening agent.

16. Name two dyes formerly obtained from vegetable sources that are now prepared from coal tar.

THOUGHT QUESTIONS

1. (*a*) Why do we color butter? (*b*) Why do we color oleomargarine? (*c*) Why do some states forbid the coloring of oleomargarine? (*d*) Do you think that a law forbidding the coloring of oleomargarine is just?

2. (*a*) What is the difference in composition between benzene and benzine? (*b*) Give the source of each. (*c*) What properties have they in common?

OPTIONAL EXERCISES

1. In Fig. 369 trace the steps in the preparation of aspirin from coal.

2. Obtain samples of different kinds of vinegars, evaporate about 50 ml of each to dryness on a water bath, and examine the residues. Exhibit the results to the class. Explain any differences in the residues.

3. How many grams of acetic acid can be prepared from 1 kg of 95 per cent alcohol?

VIII. THE FOOD WE EAT

What is food? We must have food in order to live. But to keep our bodies in health, we must also know how to select food wisely; for its value to us does not always correspond to its cost. We begin our study by asking again, "What is food, and what must it do for us?"

Food is required for at least three different purposes. It is necessary (1) to the growth of our bodies; (2) to repair worn parts (for our bodies are constantly wearing out, especially during hard muscular work); (3) to supply combustible material for the energy of work, as well as to keep up the heat of the body. Any material that meets one or more of these purposes is a food.

The different kinds of foods. So far as we know, all the elements that make up our foods are supplied in the form of a large variety of compounds, most of them very complex in character. Yet all these compounds belong to one of the following groups (sometimes called the nutrients): *carbohydrates*, *fats*, *proteins*, *mineral matter*, and *vitamins*. In addition to these, water, oxygen, and certain enzymes are necessary for life, although these are not generally regarded as foods. We have already studied the carbohydrates and fats, so that we are familiar with their composition and properties.

The *proteins* are very complex compounds of nitrogen, such as the casein of milk, the gluten of flour, and the albumin of eggs. From these proteins in our foods are built up our muscles and many other tissues of our bodies. The *mineral matter* includes the compounds of the metals, such as common salt and calcium phosphate ($Ca_3(PO_4)_2$), which is the chief constituent of our bones. Since the mineral matter in our foods is left in the form of an ash when the foods are burned, it is customary to record it simply as *ash* in giving the analyses of foods. The composition of a number of our common foods is given on the opposite page.

The vitamins help to guard our health. The vitamins are complex compounds present in many of our foods. Although we know much about them, our knowledge is still very incomplete. At least six or seven are known, and it seems certain that others will be discovered. Each one bears the name of a letter of the alphabet; at present we have vitamins A, B, C, D, E, and G, some of which include more than one vitamin. Each serves a definite purpose. Thus vitamin C prevents the disease known as scurvy, while vitamin D prevents rickets — a disease prevalent among children.

AVERAGE COMPOSITION OF EDIBLE PORTION OF TYPICAL FOODS EXPRESSED IN GRAMS PER 100 GRAMS OF FOOD*

FOOD	WATER	PROTEIN	FAT	CARBOHYDRATE	ASH	FUEL VALUE (Cal per 100 G)
Almonds (dried) . . .	4.7	18.6	54.1	19.6	3.0	640
Apples (fresh, all) . .	84.1	0.3	0.4	14.9	0.29	64
Asparagus (fresh) . . .	93.0	2.2	0.2	3.9	0.67	26
Bananas	74.8	1.2	0.2	23.0	0.84	99
Beans (dried)	12.0	25.1	1.8	57.7	3.4	347
Beans (string)	88.9	2.4	0.2	7.7	0.77	42
Beef (round, medium) .	67.0	19.3	13.0	—	0.95	194
Beef (round, fat) . . .	63.0	18.7	17.0	—	0.9	228
Beets (fresh, root) . .	87.6	1.6	0.1	9.6	1.1	46
Bread (graham, milk) .	37.0	10.0	4.0	47.0	2.0	264
Bread (white, all-milk)	36.0	9.0	3.6	49.8	1.6	268
Butter	15.5	0.6	81.0	0.4	2.5	733
Cabbage (fresh) . . .	92.4	1.4	0.2	5.3	0.75	29
Carrots (fresh, roots) .	88.2	1.2	0.3	9.3	1.02	45
Celery (stalks)	93.7	1.3	0.2	3.7	1.08	22
Chicken (total edible) .	55.9	18.0	25.0	—	1.1	297
Codfish (fresh)	82.6	16.5	0.4	—	1.2	70
Corn (sweet)	73.9	3.7	1.2	20.5	0.66	108
Eggs	74.0	12.8	11.5	0.7	1.0	158
Figs (candied)	21.0	3.5	0.2	73.7	1.6	311
Ham (lean, smoked). .	49.0	19.5	25.0	—	5.8	304
Lettuce (fresh)	94.8	1.2	0.2	2.9	0.91	18
Macaroni (cooked, plain)	75.0	3.7	0.4	19.4	1.5	96
Milk (cow, fresh) . . .	87.0	3.5	3.9	4.9	0.7	69
Oatmeal (uncooked) .	8.3	14.2	7.4	68.2	1.9	396
Oils, salad	—	—	100.0	—	—	900
Oranges (fresh)	87.2	0.9	0.2	11.2	0.47	50
Peaches (fresh)	86.9	0.5	0.1	12.0	0.47	51
Peanuts (roasted) . .	2.6	26.9	44.2	23.6	2.7	600
Peas (young)	81.4	5.4	0.3	12.1	0.77	73
Potatoes (fresh) . . .	77.8	2.0	0.1	19.1	0.99	85
Prunes (dried)	24.0	2.3	0.6	71.0	2.1	299
Raisins (seeded) . . .	24.0	2.3	0.5	71.2	2.0	298
Rice (white, uncooked)	12.3	7.6	0.3	79.4	0.4	351
Salmon (canned) . . .	67.4	20.6	9.6	—	2.4	169
Spinach (leaves) . . .	92.7	2.3	0.3	3.2	1.53	25
Strawberries (fresh) . .	90.0	0.8	0.6	8.1	0.5	41
Tomatoes (fresh red) .	94.1	1.0	0.3	4.0	0.57	23
Turnips (fresh)	90.9	1.1	0.2	7.1	0.73	35
Wheat flour (white) . .	12.0	9.3	1.0	77.2	0.5	355

---

* These values are taken from Circular No. 549, United States Department of Agriculture, issued June, 1940. The fuel values are obtained from the following formula (1 Cal = 1000 cal): Cal in 100 g = $4P + 9F + 4C$, in which P, F, and C represent, respectively, the number of grams of protein, fat, and carbohydrates in 100 g of the food.

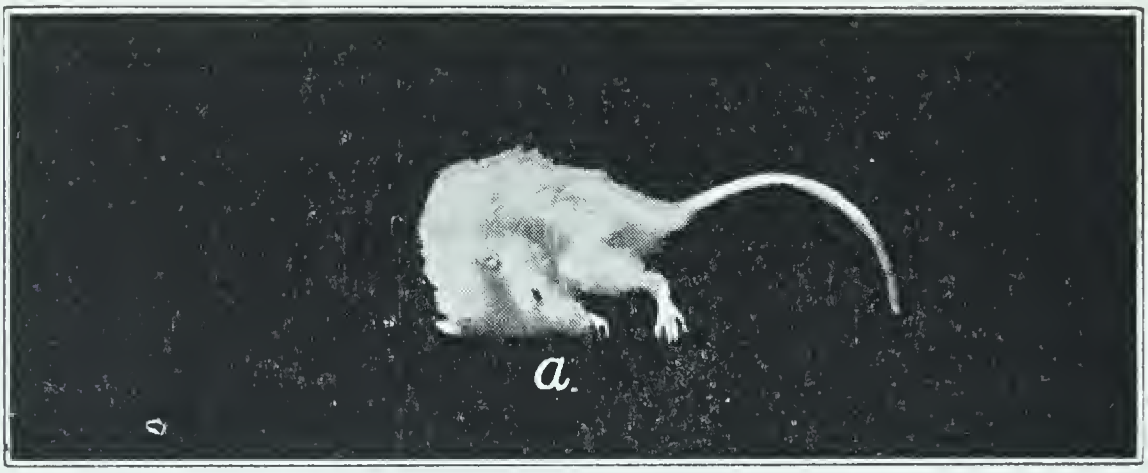


Fig. 371. Effect of deficiency of vitamin B in diet of a rat

At twenty-eight days of age the rat was placed on a diet containing but a minimum of vitamin B. It lost weight rapidly and developed paralysis, as in *a*

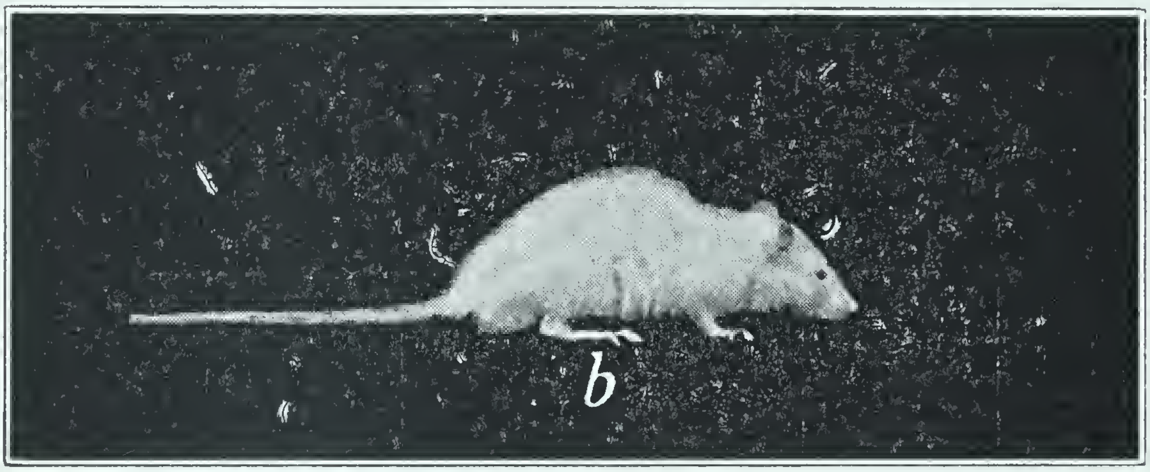


Fig. 372. Effect of renewed supply of vitamin B

A food rich in vitamin B was then fed to the rat; after twenty-four hours the symptoms of paralysis had entirely vanished, and it appeared as in *b*. (Photographs from the United States Department of Agriculture)

Foods vary in the amounts and kinds of vitamins present, but the percentage is always very small. All are present to some extent in milk and green vegetables. Citrus fruits are a good source of vitamin C; cod-liver oil, of vitamin D; and yeast, of vitamin G. Vitamin D is also formed in our bodies when they are exposed to sunshine.

Because of their wide occurrence in fresh vegetables, milk and dairy products, and some meats, anyone whose diet is made up of a mixture of these is certain to obtain an adequate amount of vitamins. Some of them have been obtained in a pure state and may be purchased in concentrated form at our drug stores. Fig. 373 gives some information about the sources and effects of these important compounds.

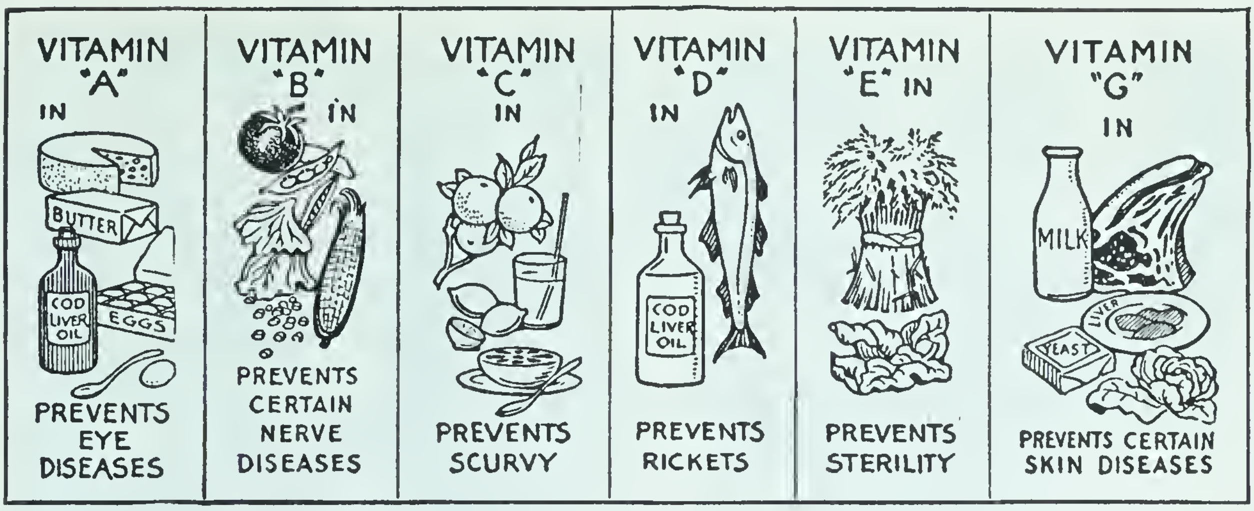

VITAMIN "A" IN
BUTTER
COD LIVER OIL
EGGS
PREVENTS EYE DISEASES
VITAMIN "B" IN
PREVENTS CERTAIN NERVE DISEASES
VITAMIN "C" IN
PREVENTS SCURVY
VITAMIN "D" IN
COD LIVER OIL
PREVENTS RICKETS
VITAMIN "E" IN
PREVENTS STERILITY
VITAMIN "G" IN
MILK
LIVER
YEAST
PREVENTS CERTAIN SKIN DISEASES

Fig. 373. Sources of vitamins

Drawing after *Science News Letter*

The service rendered by each class of foods. The particular service rendered by each class of foods is given below:

Kind of Food	Chief Service Rendered	Occurs Especially in
Proteins	Build muscle and other tissues and repair worn-out parts. Will furnish energy in the absence of fats and carbohydrates	Lean meats, eggs, milk, cereals, dried beans, peanuts, codfish, and salmon
Fats	Maintain the body temperature, and furnish energy to do work	Butter, lard, vegetable oils, pork, peanuts, eggs, chicken, fat meats
Carbohydrates . .	Similar to that of the fats	Sugar, wheat flour, bread, rice, cereals, figs, raisins
Minerals	Build bones and teeth; constituent of compounds present in muscles and blood; regulate such processes as clotting of blood, activity of muscles and nerves, and oxidation	Smoked bacon and ham, butter, bread, dried beans, figs, oatmeal, milk, eggs, prunes, raisins, and spinach
Vitamins	See Fig. 373	See Fig. 373

While the fats and carbohydrates, and, to a certain extent, the proteins, are interchangeable, experiments prove that a proper mixture of these foods is essential to health. Of course it is true that one can live for many days on one kind of food, especially protein; in fact, persons have lived for a month or more without any food whatever, other than water. In all such cases the necessary materials are derived from the surplus supply always stored up in the normal body.

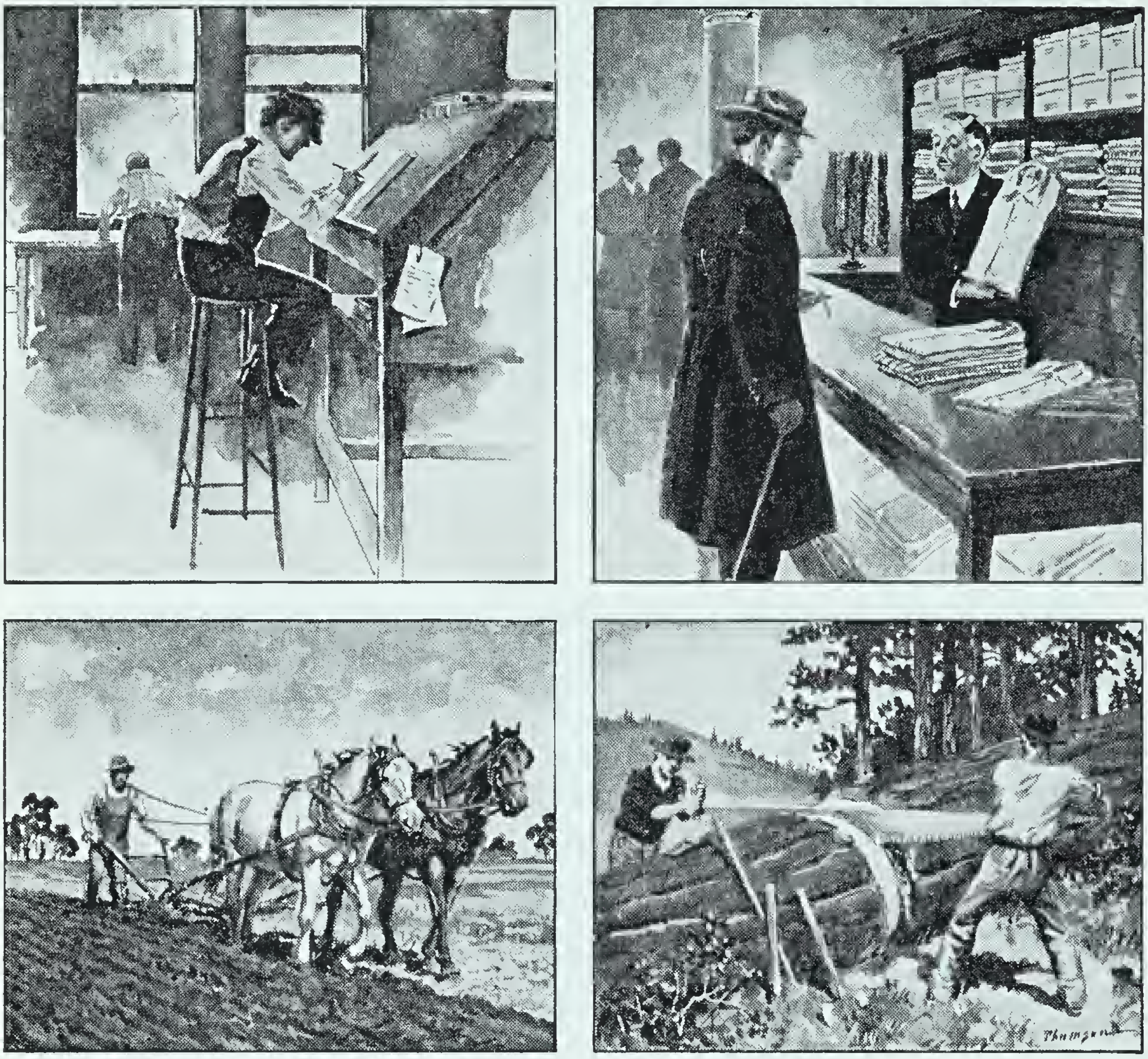


FIG. 374. Calculate the approximate calorie requirements per hour for each of the persons shown prominently in the above pictures

Energy value of foods. Experiments show that the heat of the body, as well as the energy used in muscular work, comes from the oxidation of food. Indeed, most of our foods may be thought of as fuel. So in the study of foods it is convenient to use their *fuel values* (heats of combustion) in comparing the value of one with that of another. These values are measured in the *calorimeter* (Fig. 35) in *large* calories (Cal), which are 1000 times as large as the small calorie (cal).

Experiments show that our bodies get from the carbohydrates, fats, and proteins, when these are dissolved by digestion and oxidized, approximately the following fuel values:

CLASS OF FOODS	CALORIES PER GRAM	CALORIES PER POUND
Carbohydrates	4	1815
Fats	9	4082
Proteins	4	1815

Amount and nature of foods necessary for health. Many studies have been made to find out just how much and what kind of food is best adapted for healthy living. Evidently many conditions enter into the problem, such as one's age, weight, and occupation, and the climate in which one lives.

In stating food requirements for a period of, say, twenty-four hours it is necessary only to give the weight of protein needed, together with the total fuel value. For the fats and carbohydrates have nearly the same function. The difference between the total fuel value and that of the needed protein gives the number of Calories to be supplied from fats and carbohydrates. A mixture of these two food materials is selected such that its fuel value, together with the fuel value of the protein, equals the total fuel value required.

Different dietary standards have been proposed; but the following ones, recommended by a committee of food experts in 1936, are generally accepted. They give the food requirements for a period of twenty-four hours.

1. *The twenty-four-hour protein requirements in grams per kilogram of body weight.* This requirement is proportionally greater in the growing child than in adults. For children from one to three years, the intake should be about 3.5 g, gradually diminishing to 1 g for adults of twenty-one years of age and upwards.
2. *The twenty-four-hour calorie requirements.* For an adult living an ordinary, everyday life in a temperate climate, and not engaged in manual work, 2400 Calories are sufficient. If one is engaged in muscular work, there should be added to this from 75 to 300 Calories per hour of work, depending upon how much work is done. Children require proportionally less, beginning with about 840 Calories at one year of age and gradually increasing to 2400 at fifteen years of age. (Fig. 374.)

Pure Food and Drug Act. In 1906 the Federal Congress passed what is known as the Pure Food and Drug Act. This fixes the standard of various foods and drugs, and directs that all labels must tell the truth and must state the presence of any dangerous or habit-forming drugs. The effect of the act may be seen by a study of Fig. 375, which shows the label used on a well-known patent medicine before the act was passed and how it had to be modified to meet the requirements of the act. This act, amended in 1938, has accomplished much good, but needs further strengthening.

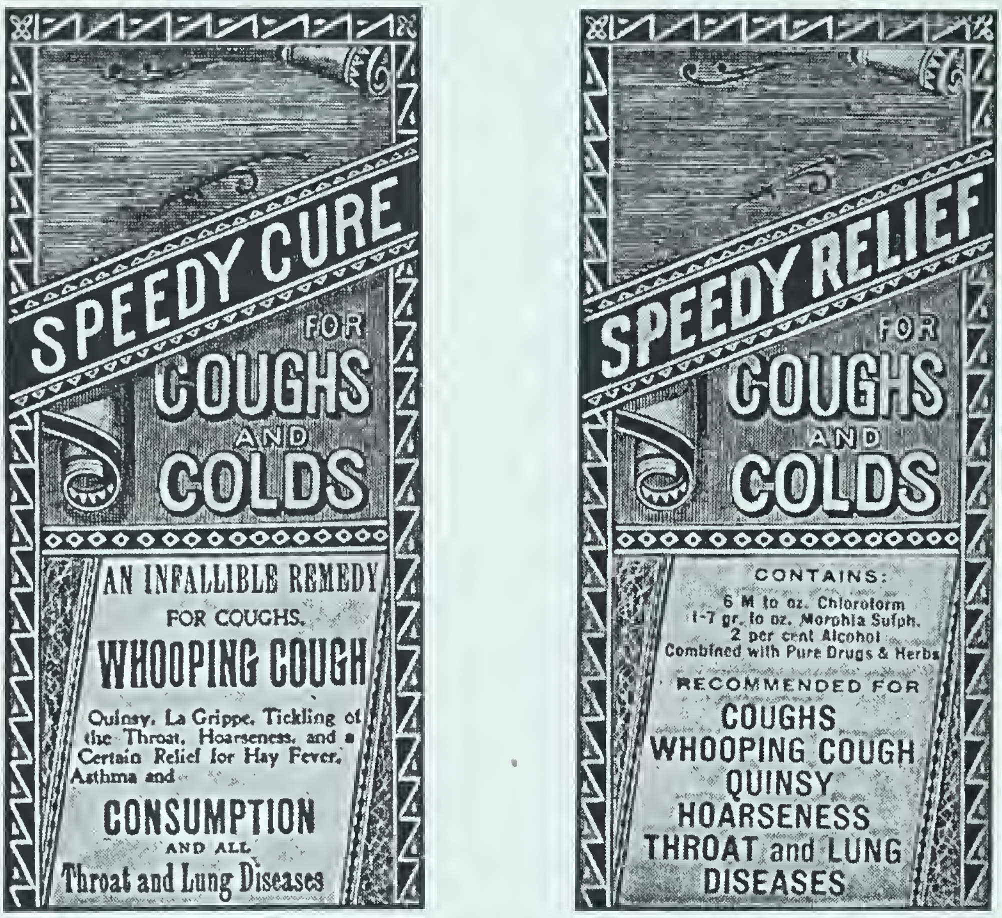

SPEEDY CURE
FOR
COUGHS
AND
COLDS
AN INFALLIBLE REMEDY
FOR COUGHS,
WHOOPING COUGH
Quinsy, La Grippe, Tickling of the Throat, Hoarseness, and a Certain Relief for Hay Fever, Asthma and
CONSUMPTION
AND ALL
Throat and Lung Diseases
SPEEDY RELIEF
FOR
COUGHS
AND
COLDS
CONTAINS:
6 M to oz. Chloroform
1-7 gr. to oz. Morphia Sulph.
2 per cent Alcohol
Combined with Pure Drugs & Herbs
RECOMMENDED FOR
COUGHS
WHOOPING COUGH
QUINSY
HOARSENESS
THROAT and LUNG
DISEASES

Fig. 375. The label on a well-known patent medicine before and after the passage of the Pure Food and Drug Act

SUMMARY OF PART VIII IN QUESTION FORM

1. What is a food?

2. Referring to the tables on pages 491 and 493, answer the following questions:
(*a*) What components must a satisfactory diet provide?
(*b*) What foods are rich in protein?
(*c*) What foods are rich in fats?
(*d*) What foods are rich in carbohydrates?
(*e*) What is the special function of each class of foods?
(*f*) What common function have protein, fats, and carbohydrates?

3. One of the purposes for which food is taken into the body is to release energy. (*a*) Which kind of food releases energy in relatively large amounts? (*b*) What unit is used to measure the fuel values of food?

4. Consult page 495 and note the approximate number of Calories per day you need.

5. Name the class of foods and the vitamin present in abundance in each of the following foods: (*a*) eggs; (*b*) butter; (*c*) meat; (*d*) tomatoes.

6. Why do we associate certain foods, such as bread and butter, ham and eggs, oatmeal and cream? (Consult the table on page 491.)

7. What weight of water are you buying when you buy 10 lb of (*a*) apples? (*b*) string beans? (*c*) butter? (*d*) peaches? (*e*) tomatoes? (*f*) spinach? (*g*) celery?

8. What action did the Federal government take in 1906 and again in 1938 to aid you in improving your diet and your health?

UNIT READINGS

BEERY. *Stuff.* [Chapter V tells of foods; Chapter X, of textiles of all kinds and of dyes. Simple and interesting.]

BENSON. "The Story of Paper," *Journal of Chemical Education*, Vol. VII, pp. 1739–1762. [An excellent article, with good illustrations.]

FOSTER. *The Romance of Chemistry.* [Chapter XXIV, "The Housewife's Dependence on Chemistry," tells about foods.]

HOLMES. *Out of the Test Tube.* [Chapter XVII, "Silks and Cellulose"; Chapter XXII, "Sugars and Sweetness"; Chapter XXIII, "Fats to the Front"; Chapter XXIV, "Now What Shall We Have to Eat?" All brief, simple, and interesting.]

HUSSEY and SCHERER. "Rayon — Today and Tomorrow," *Journal of Chemical Education*, Vol. VII, pp. 2543–2570.

McGLUMPHY and EICHINGER. "Levulose, the Sugar of the Future," *Journal of Chemical Education*, Vol. X, pp. 453–463.

SADTLER. *Chemistry of Familiar Things.* [Chapters XIII and XIV tell about foods.]

SCHERER. "Cellulose and its Place in Industry," *Journal of Chemical Education*, Vol. X, pp. 131–140. [Very interesting and well illustrated.]

SHERMAN. *Chemistry of Food and Nutrition.* [A standard treatise on the subject, and somewhat comprehensive. The student will enjoy studying the tables in the appendix giving the composition of the various foods and the vitamins present in each of the different foods.]

SLOSSON. *Creative Chemistry.* [Chapter IX, "The Rival Sugars"; Chapter X, "What Comes from Corn"; Chapter XI, "Solidified Sunshine." All of interest; the stories are told in an attractive way.]

TILDEN. *Chemical Discovery and Invention in the Twentieth Century.* [Chapter XX, "Coal Tar," is good but somewhat advanced.]

The Science Leaflet. [No. 11 of recent volumes tells of foods; No. 12, of organic compounds of carbon; and No. 13, of products made by synthesis, most of which contain carbon.]

The World Book Encyclopedia. [Contains excellent and well-illustrated discussions under "Food," "Paper," "Sugar," "Coal" (this includes coal tar), and "Dynamite."]

Unit Twelve. Metals — Pure, Mixed, and in Compounds

HAVE you ever thought how many metals we use every day in one form or another? You can think of many uses of iron at once, but you may forget — if you ever knew it — that in general this is not pure iron. For special purposes it may have in it quite a variety of metals, such as manganese, chromium, nickel, cobalt, vanadium, or tungsten.

The coins we use are made of gold, silver, nickel, or copper. The brass ornaments are copper and zinc; the kitchen pans are aluminum. The wiring of the house is copper; at least some of the plumbing is lead. The cans we open for our preserved fruits and vegetables are iron, tin, and lead; the wire in the electric lamp is tungsten. The teaspoons are silver.

The type for our books contains antimony; the plating on our automobile is apt to be copper, nickel, and chromium; the frame of the airplane is made of aluminum and magnesium. The lady's jewelry is likely to be gold, platinum, or palladium. The moving column in the thermometer is mercury.

Where do all these metals come from? In what form are they found in nature? How are the pure metals got from their minerals? What compounds do these metals make that are of use to us, and how do we get them?

Questions about these things that so enrich our lives are full of interest, and this unit will be given up to answering some of them so far as they apply to *all* metals.

CHAPTER XL

What the Metals Are, and How We Get Them

[Nature Gives Us Few Free Metals. We Get Them from Ores]

What do you know about metals? Everyone knows a few metals by sight. Gold, silver, iron, copper, lead, tin, need little description of what they look like. These give us our usual idea of what a metal is: a material that is heavy, hard, shining, and not easily melted. Yet many metals are light in weight, a few melt below the boiling point of water, and a number are soft enough to be cut with a knife like cheese.

All that the ordinary person knows about how we get the metals is that gold is found in sand, and iron is made from iron ore in a blast furnace. Few know anything about the chemical conduct of metals beyond the fact that most of them rust or tarnish in air while a few, like gold or chromium plate, do not. So there is much to be learned about metals.

What metals are like. With the exception of gold and copper, all metals look like silver or tin; and all polish to a mirrorlike surface, or *luster*. All are strongly crystalline, with sharp melting points, and in differing degrees are good conductors of heat and electricity. At ordinary temperatures all are solids, except mercury, which melts at – 38.9°; but in melting point they range from about 30° to more than 3000°.

Most familiar metals are heavy, but some others are very light (Fig. 376). Most of them can be drawn into fine wire (are *ductile*) or rolled or hammered into thin sheets (are *malleable*); but some metals have neither of these properties to any great extent. So no general description fits all the metals.

How the metals act. Most of the common metals combine easily with oxygen, chlorine, or sulfur, and for this reason their surface tarnishes on continued exposure to air. Those that do not tarnish, such as gold or platinum, are sometimes called *noble* metals.

The metals above hydrogen in the electromotive series (p. 261) act on dilute acids and set free hydrogen from them.

Those below hydrogen do not act in this way; but many of them are first oxidized by concentrated acids, and their oxides then react with the acids to form salts (p. 299).

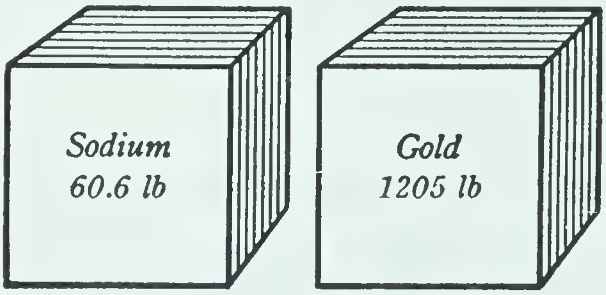


FIG. 376. Weight of 1 cu ft of sodium and of gold

Hydroxides of metals are bases. We have defined a metal as *an element whose oxide is a basic anhydride* (p. 304). Since these anhydrides unite with water to form a base, we may also define a metal as *an element whose hydroxide is a base.* When the hydroxide of a metal, or any of its simple salts, is dissolved in water, the metal atoms act as simple positive ions.

Atoms of metals lose electrons easily. The atoms of hydrogen and of the metals have few electrons in their valence orbits, and give these up easily to form electrovalent compounds:

$$\mathrm{Ca}\!:+\,\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}\!:\longrightarrow \mathrm{Ca}^{++},\,:\!\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}\!:^{--}$$

It is owing to these easily detached electrons that the metals are good electrical conductors.

Because the metallic atoms lose their valence electrons easily, they are good *reducing agents*; for loss of electrons means that they are oxidized (p. 207). So metals are easily acted on by such oxidizing agents as oxygen and chlorine.

How metals are found in nature. Very few metals except gold and copper are found in nature as free metals. They are combined with other elements in the form of various compounds called *minerals.* These minerals are usually scattered as small crystals through various rocklike materials as a mechanical mixture (Fig. 377). Any natural material from which a useful element or compound can be made is called an *ore* of that element or compound. The process of winning a metal from its ore is called *metallurgy.* It usually requires two general steps: (1) ore-dressing; (2) smelting.

Ore-dressing. Window-dressing is displaying the goods of a store in its show windows so as to make the best impression on the shopper. Ore-dressing is preparing the ore as well as possible for getting the metal out of it. For, as a rule, we cannot at once start on the work of getting a metal from an ore as we find it in nature. The ore may contain only a small percentage of the useful mineral mixed up with a large percentage of useless material, like sand, clay, or rock of some kind. There may also be substances present that would interfere with getting the desired metal from the ore.

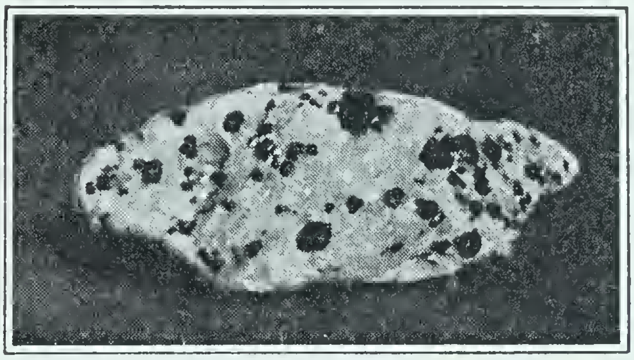


FIG. 377. A dark-colored mineral in quartz

So the useful mineral must be separated from the worthless, — at least partially, — or *concentrated*, as a first step. This concentration process is called *ore-dressing*. This may be done in a number of ways, depending on the ore used. Two methods will be described briefly.

Concentration by washing. The stonelike material in which the valuable metallic minerals are embedded is rarely as heavy as are the mineral particles. So the ore is crushed to rather fine particles and then stirred in running water. The lighter, worthless particles are washed away, while the heavier ones are left behind as a mineral concentrate.

Concentration by flotation. There is another ingenious method, called the *flotation* method, that works especially well for low-grade sulfide ores. The finely crushed ore is churned into a froth with water and a little oil of some kind (often pine oil).

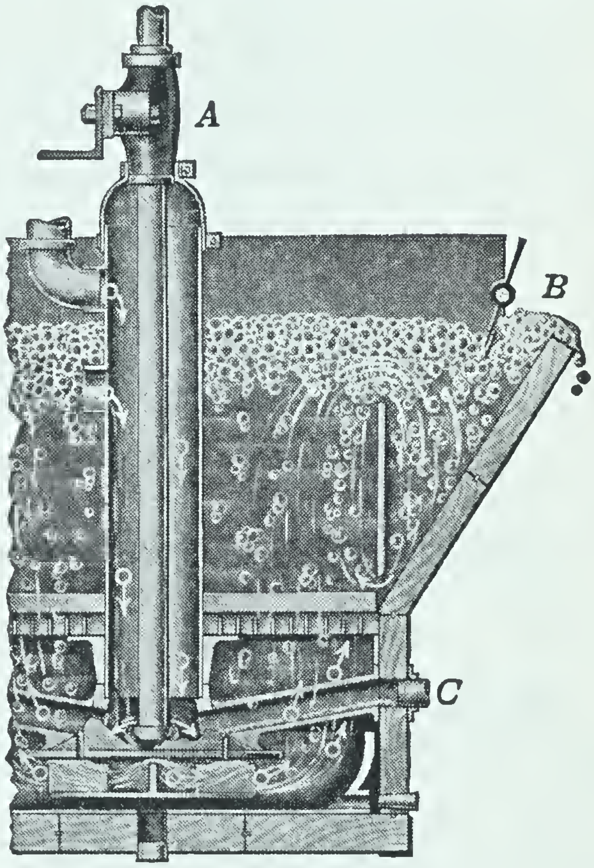


FIG. 378. The flotation process

Powdered ore, water, oil, and air are delivered into the shaft *A* and beaten to a froth by the fan at the base of the shaft. Air bubbles carrying the ore rise as a froth and overflow at *B*. The worthless materials are driven off through *C*

Now the particles of sulfide minerals, free metals like gold, and some other minerals as well are much heavier than water. But when churned with water and oil, the mineral particles attach themselves to air bubbles and are carried up into the froth, like the heavy gondola of an airship carried up by the big gas bag. The froth, with its valuable burden, is skimmed off the top (Fig. 378), and the concentrated mineral is recovered from it.

Smelting — Getting a metal from its concentrated ore. Even the best concentrates, or the purest natural ores, contain undesirable materials. Some of these can be removed by a special *chemical* treatment called *roasting*; others must be removed later in the operation of *reduction* of the ore. These two processes, roasting and reduction, are together called the *smelting* of the ore.

Roasting. Roasting is heating the ore in the open air to a moderately high temperature. This is to get rid of anything that can be converted into a gas and so driven off.

A hydrated oxide may lose all possible water:

$$2\ Fe(OH)_3 \longrightarrow Fe_2O_3 + 3\ H_2O\uparrow$$

Carbonates are decomposed, and often oxidized as well:

$$4\ FeCO_3 + O_2 \longrightarrow 2\ Fe_2O_3 + 4\ CO_2\uparrow$$

Some sulfides are burned to form oxides:

$$4\ FeS_2 + 11\ O_2 \longrightarrow 2\ Fe_2O_3 + 8\ SO_2\uparrow$$

Reduction of an ore. Reduction is the final step in getting the more or less pure metal from the ore as made ready by concentration and roasting. Each kind of ore must have special treatment to get rid of the remaining earthy or stony impurities. But the general *plans* of reduction can be stated very briefly.

Reduction of an oxide by carbon. Many oxides, when heated with carbon, are reduced to the metal, with the formation of carbon dioxide (at rather low temperatures) or carbon monoxide (at high temperatures):

$$2\ CuO + C \longrightarrow 2\ Cu + CO_2\uparrow$$
$$Fe_2O_3 + 3\ C \longrightarrow 2\ Fe + 3\ CO\uparrow$$

Reduction of an oxide by aluminum. Aluminum has a great affinity for oxygen and is now a relatively cheap metal. Some oxides that cannot be reduced successfully by carbon can be reduced by heating them with aluminum:

$$Cr_2O_3 + 2\,Al \longrightarrow 2\,Cr + Al_2O_3$$

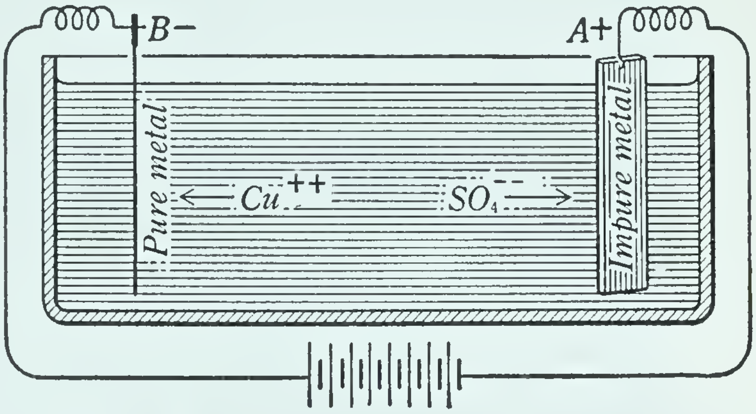


Fig. 379. The refining of copper by electrolysis

Reduction by electrolysis. The method of reduction easiest to understand is that of electrolysis. A suitable easily-melted compound of the metal is melted, and an electric current is passed through the liquid compound. The anode is usually made of carbon rods, and the cathode is made of the pure metal. When an electric current passes through the melt, the metal is deposited on the cathode.

$$Mg^{++},\ Cl^{-}{}_2 \longrightarrow Mg + Cl_2\uparrow$$

Metals that do not act on water, or act very slowly, can be got by electrolysis of a water solution of their salts.

Purification of metals. It is usually true that metals reduced in these ways (except by electrolysis) are still somewhat impure. Metals that act on water easily, like magnesium, are nearly always obtained by electrolysis of melted salts and are pure enough for most uses. Other metals can be purified, or refined, by electrolysis of a solution of a suitable salt.

For this purpose the impure metal is made into a heavy anode *A* (Fig. 379), with a thin cathode *B* of pure metal. The electrolyte is a solution of some convenient salt — say the sulfate. As the current passes through the solution the metal is dissolved from the anode and deposited on the pure cathode. The impurities in the anode either drop down in the cell as insoluble material or stay dissolved in the electrolyte.

Electroplating. A thin layer of one metal is often deposited on the surface of a different metal by electrolysis. This process is called *electroplating*. It is done to protect the

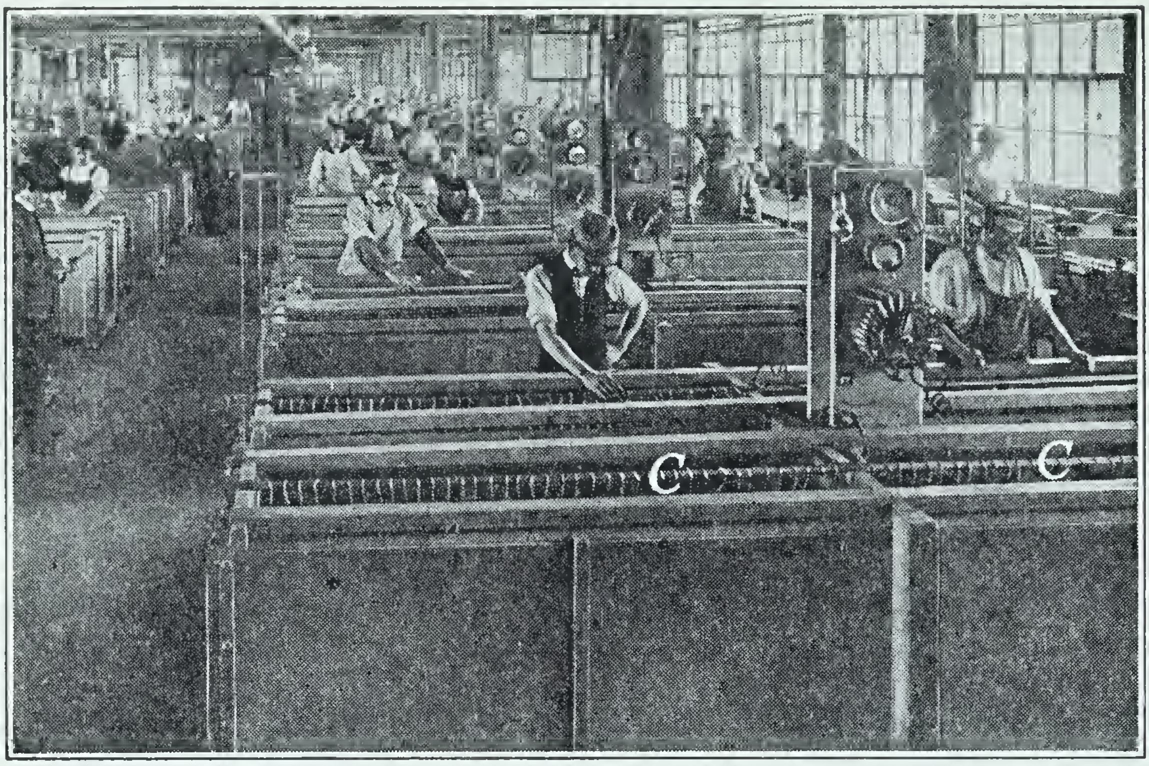


Fig. 380. The process of electroplating with nickel, as carried out in a large factory

The objects to be plated are suspended from the rods *C*, *C*, and serve as the cathode. They dip into a solution of a nickel salt, which is the electrolyte. A plate of nickel forms the anode

surface of an object from rust or tarnish, or to make it more pleasing in appearance. Everyone has seen objects plated with gold, silver, nickel, or chromium.

The object to be plated is hung by wires or rods in a solution of a salt of the metal to be deposited. The object acts as the cathode of the cell. The anode is made of the plating metal. The current dissolves metal from the anode and deposits it on the cathode. (Fig. 380.)

CHAPTER SUMMARY IN QUESTION FORM

1. (*a*) What do the metals look like? (*b*) Can you tell a metal by its looks?

2. (*a*) With what elements do most of the metals combine? (*b*) How do they react with acids? (*c*) What causes a metal to tarnish?

3. Are any of the metals liquid at ordinary temperatures?

4. How would you define *metal* (*a*) for one who had never studied chemistry? (*b*) for a chemist?

5. How do you account for the fact that most metals act as reducing agents?

6. (*a*) In what forms are the metals found in nature? (*b*) Distinguish between *minerals* and *ores*. (*c*) How are the ores concentrated?

7. Give the general methods for separating a metal from its ores, illustrating each by an example.

8. Illustrate, by a drawing, the process of electroplating.

THOUGHT QUESTIONS

1. Give an example of each of the following: (*a*) a metal so light that it will float on water; (*b*) a heavy metal; (*c*) a metal that quickly tarnishes in air; (*d*) a metal that slowly tarnishes in air; (*e*) a metal that is not acted upon by air; (*f*) a metal that liberates hydrogen from sulfuric and hydrochloric acids; (*g*) a metal that does not liberate hydrogen from acids.

2. Why cannot sodium be prepared by the electrolysis of a solution of its salts?

3. What is the advantage of electroplating?

4. (*a*) Is the most abundant element always the cheapest? (*b*) Is there any relation between the price of a metal and its *real* value to us?

CHAPTER XLI

Alloys of the Metals

[More Useful than the Pure Metals]

Pure metals are little used. If you look carefully at the metal objects in daily use, you will find that few of them are pure metals. The aluminum ware in the kitchen and the copper electrical wires are about all, and both of these as pure metals belong to the electrical age. Vast quantities of *nearly* pure iron are used annually, but, as we shall see, perfectly *pure* iron has few uses. At least small quantities of other elements must be in the iron to make it suited to most of the various uses to which it is put.

To be sure, pure gold or silver or nickel or chromium is often plated as a thin layer on other metals. Tin or zinc is melted or plated on iron. But few objects are made wholly from any one metal.

Alloys. Nearly all the metallic objects we use or see are made of at least two metals. These are melted together and allowed to solidify, and the product so made is called an *alloy.* Sometimes a nonmetal, such as phosphorus, silicon, or carbon, is melted with a metal to form an alloy.

Coins of all kinds are alloys, as is the metal of jewelry, silver plate, bronze, brass, solder, pewter, and nearly all the parts of machinery, such as an automobile (Fig. 381) or an airplane. We get the pure metals largely in order to make alloys from them.

Will metals mix in all proportions? When two melted metals are mixed together, they act much like any other pair of liquids.

1. Some liquid metals mix in all proportions, like alcohol and water. This is true of antimony and lead, gold and silver, copper and nickel.

2. Some metals have a limited solubility, each in the other, like ether and water. If more of either one is added than can completely dissolve in the other, the liquid mixture separates into two layers. The lighter one floats on the heavier like cream on milk. Lead and zinc are a pair of this kind.

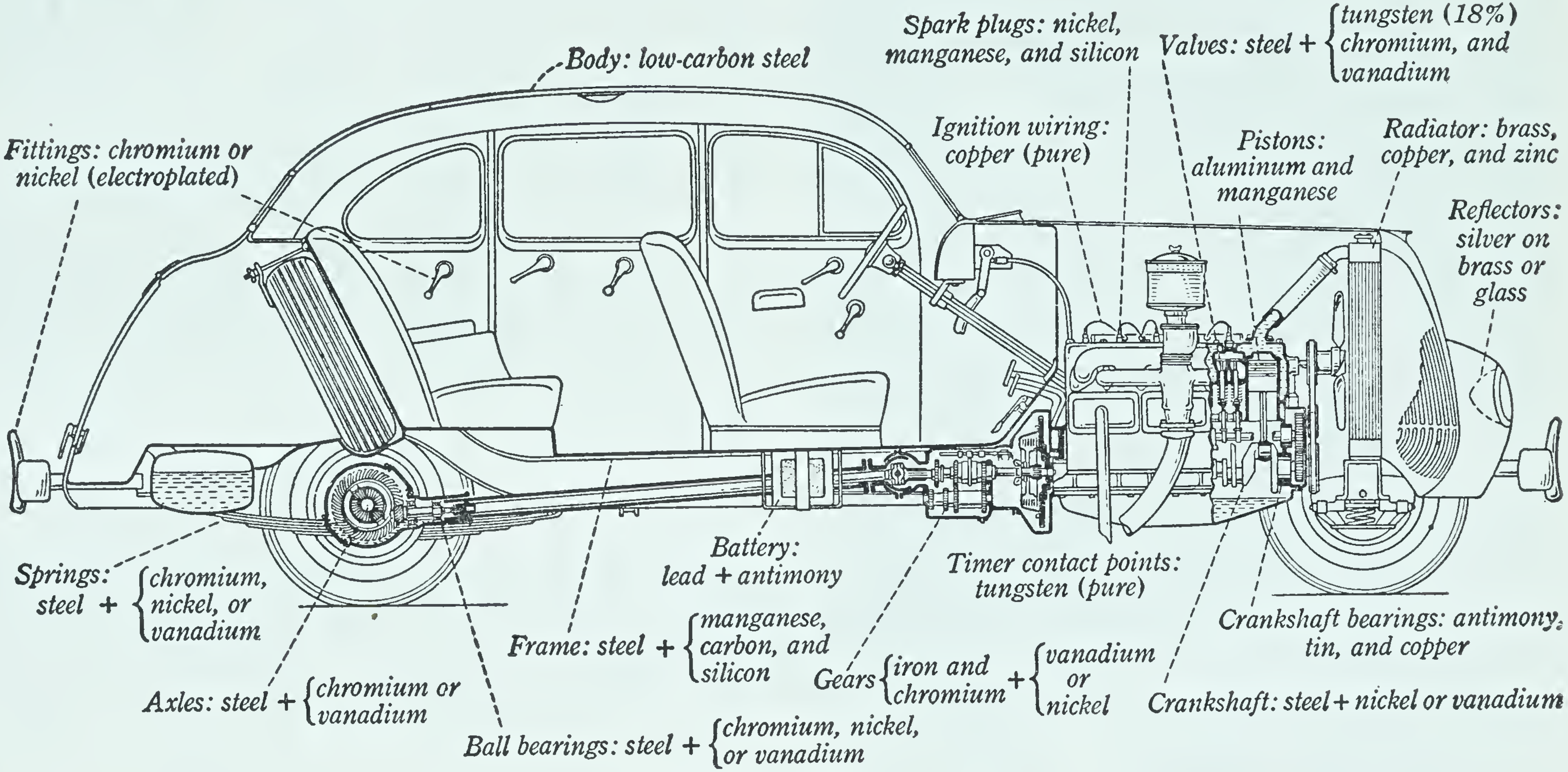

Body: low-carbon steel
Spark plugs: nickel, manganese, and silicon
Valves: steel + {tungsten (18%) chromium, and vanadium
Fittings: chromium or nickel (electroplated)
Ignition wiring: copper (pure)
Pistons: aluminum and manganese
Radiator: brass, copper, and zinc
Reflectors: silver on brass or glass
Springs: steel + {chromium, nickel, or vanadium
Battery: lead + antimony
Timer contact points: tungsten (pure)
Crankshaft bearings: antimony, tin, and copper
Frame: steel + {manganese, carbon, and silicon
Gears {iron and chromium + {vanadium or nickel
Axles: steel + {chromium or vanadium
Crankshaft: steel + nickel or vanadium
Ball bearings: steel + {chromium, nickel, or vanadium

FIG. 381. Diagram showing some of the alloys used in the construction of an automobile

What happens when we cool a mixture of melted metals? When a mixture of two melted metals is cooled, crystals begin to form at some definite temperature. As the temperature falls, more and more of the liquid crystallizes until all of it has frozen to a solid mass made up of various kinds of crystals.

The solid alloy so formed may consist of (1) a mixture of crystals of the two pure metals; or (2) crystals of the *compounds* of the two metals, for two metals may combine to form definite compounds. Or (3) every crystal in the alloy may be like every other one and may be made up of the two metals in about the proportion in which they were present in the melt.

Any or all of these types of crystals may be present in the solidified alloy. So alloys show a wide variety in their structure, depending on the character of their crystals, their relative proportion, their size, and the way in which they are packed together.

Low-melting alloys. We have seen that the freezing point of a liquid is lowered by dissolving a solid in the liquid (p. 72). In just this same way the freezing point of liquid lead is lowered by dissolving antimony in the lead; and the freezing point of antimony is lowered by dissolving lead in the antimony. If we melt the two metals together in about the proportion of their atomic weights, we get a liquid that solidifies to an alloy whose general melting point is below that of either of the two metals.

If we add a third metal of relatively low melting point to the melt, we shall get a still lower-melting alloy. Some such alloys will melt if dipped in boiling water.

Properties of alloys. As a rule the properties of an alloy cannot be predicted at all closely from those of the two metals. It is true that the density of the alloy is apt to be a rough average of that of the two metals. It seems reasonable that the reddish copper alloyed with silvery zinc should give yellow brass. But silvery nickel entirely overcomes the reddish tint of copper, as is seen in our five-cent coins, which are three-quarters copper. Both silver and cadmium (a metal that looks like zinc) give gold a greenish tint.

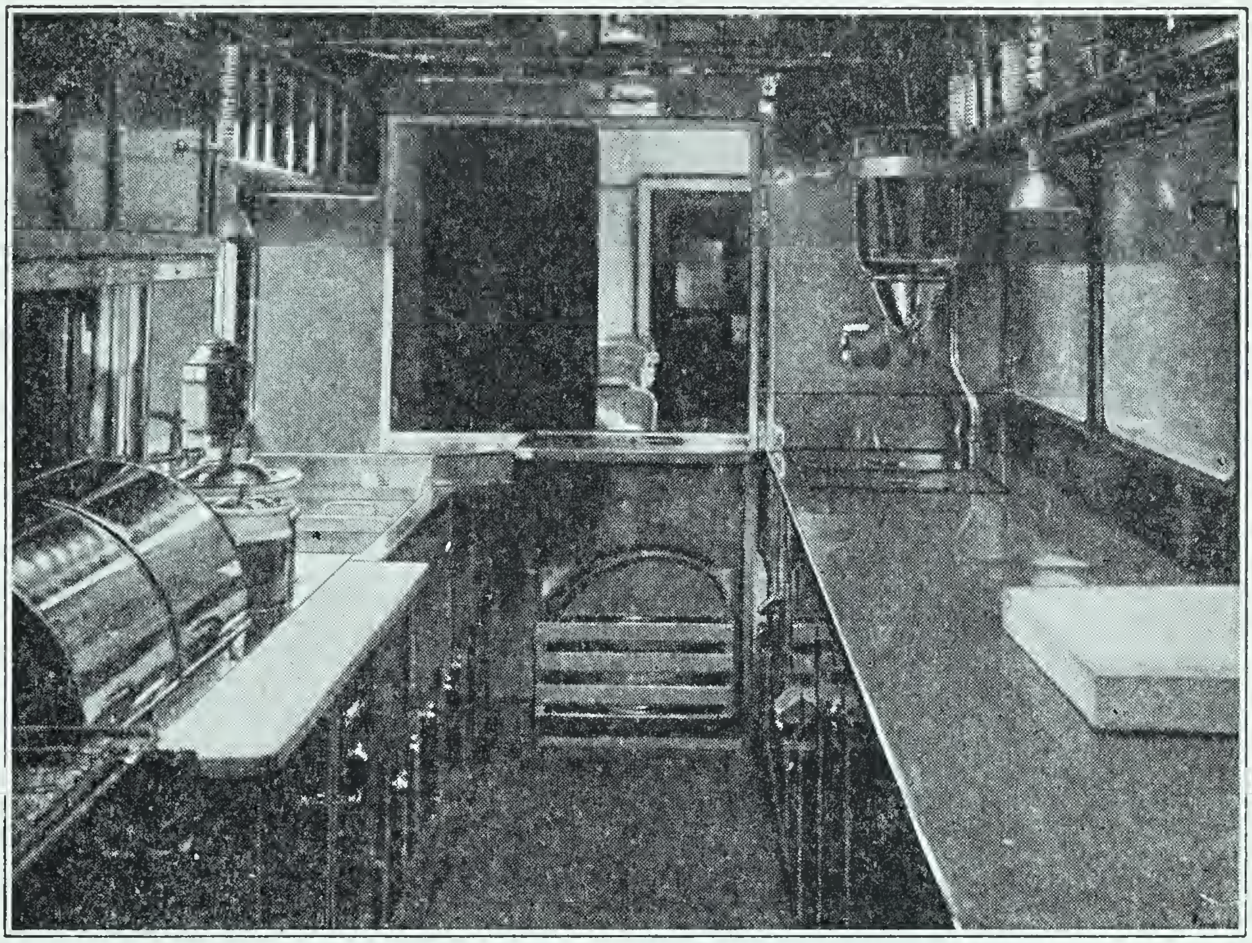


FIG. 382. The kitchen in a railroad dining car. All parts are made of a nonrusting alloy known by the trade name of *monel metal*

An alloy is usually harder than either of the metals in it, and the electrical resistance is much greater. For this reason most kinds of resistance wires are alloys. Many alloys resist chemical action better than either component metal.

Why are alloys so important now? We live in an age of machines and all sorts of metal devices. Our homes are full of them, from the front-door bell to the ash can in the alley. And almost every machine, every one of its parts, every metal object we use, calls for special metal properties that no pure metal has. Some parts of a machine must be hard, others soft; some must be heavy, others light; some rigid, others flexible, still others elastic; and so on through a long list of demands.

Hence literally thousands of alloys have been made and given trade names, each alloy with some property adapted to a definite use. Thousands more can be made with properties no one can foretell. Some large firms keep up laboratories for alloy study, and make an alloy having almost any desired properties. Many rarer metals that have never found a special use are being studied very carefully, largely to see what properties they will give to alloys of other metals.

Alloys of antimony and bismuth. These two are heavy, low-melting metals (p. 378), and are much used in various kinds of low-melting alloys. Unlike some metals, antimony expands as it freezes, and many of its alloys share this property. This is why it is used in the antimony-lead alloy called *type metal.* A metal that froze with *contraction* would harden fitting loosely and inexactly to the mold. An *expanding* alloy hardens with a snug fit, and the lines are sharp-cut. Antimony is too brittle and high-melting to be used alone.

The alloys of bismuth melt at very low temperatures. So they are used in safety links or plugs in fire extinguishers (Fig. 383), safety plugs in boilers, and fuses of various kinds.

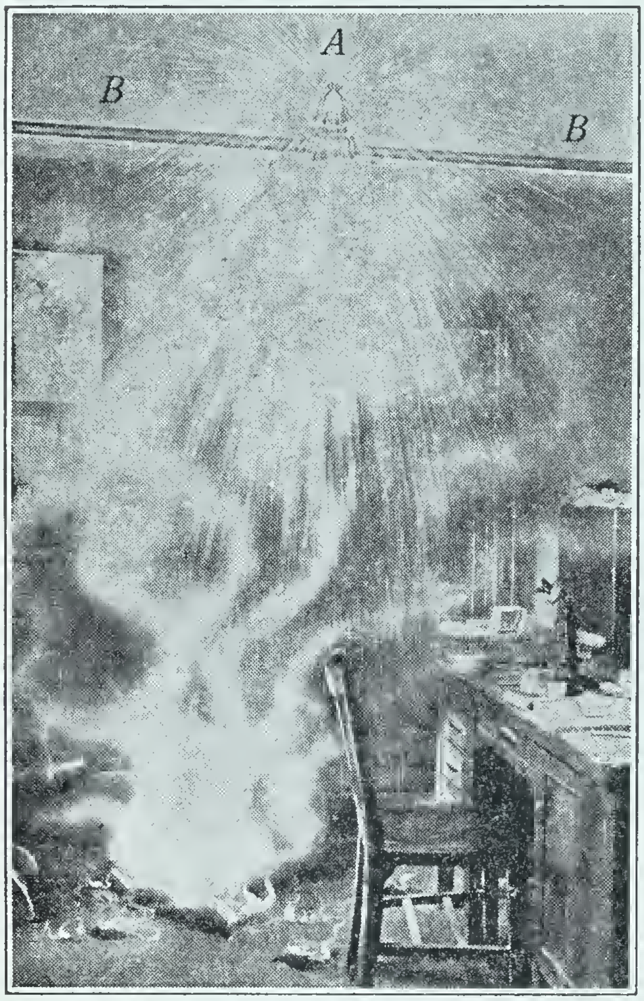


FIG. 383. An automatic fire extinguisher

The picture shows a fire that started at night in an office building. The heat of the fire soon melted the fire plug *A* (made of low-melting alloy) that sealed the water pipe *B*, *B*, placed just under the ceiling. The water thus set free fell in the form of a spray over the fire and at the same time set off an automatic fire alarm

CHAPTER SUMMARY IN QUESTION FORM

1. (*a*) What is an alloy? (*b*) Give examples of common alloys.

2. (*a*) In what ways may two melted metals act when mixed together? (*b*) What happens when the mixture cools?

3. What does the solid alloy consist of?

4. Do alloys have sharp melting and freezing points?

5. Discuss alloys under the following heads: (*a*) properties; (*b*) uses; (*c*) number.

6. What properties do antimony and bismuth give to an alloy?

CHAPTER XLII

Compounds of the Metals

[By a Few Methods We Can Make a Great Many Compounds]

How many compounds of the metals are there? It will not take much thinking to see that there are a great many. With some exceptions, each metal will combine with each nonmetal — say, 60 metals times 20 nonmetals, or 1200 of the simplest of binary compounds. But most metals have at least two oxides, or chlorides, or sulfides, and so on. This would certainly double the number to, say, 2400; and we are still counting only binary compounds.

So it is quite impossible (and needless) to try to learn about all these thousands of compounds. But in this chapter we can gather together the more usual ways in which compounds may be made, and in later chapters we shall describe a few of the most useful ones.

How simple binary compounds are made. The simplest way to make such compounds is by direct union of the metal with the nonmetal. We have had many examples of such reactions:

$$3\,Fe + 2\,O_2 \longrightarrow Fe_3O_4$$
$$Cu + S \longrightarrow CuS$$
$$2\,Sb + 3\,Cl_2 \longrightarrow 2\,SbCl_3$$

A second way is by displacing one nonmetal by another:

$$2\,CuS + 3\,O_2 \longrightarrow 2\,CuO + 2\,SO_2$$
$$2\,NaI + Cl_2 \longrightarrow 2\,NaCl + I_2$$

A third way is by decomposing some suitable salt:

$$CaCO_3 \longrightarrow CaO + CO_2$$
$$2\,KClO_3 \longrightarrow 2\,KCl + 3\,O_2$$

How hydroxides are made. Hydroxides are a very important class of compounds; for they are the *bases* from which salts are formed. Most of them are insoluble in water; so we can precipitate them. To get a given one of these — say, copper hydroxide — we need only add a soluble hydroxide to a solution of any soluble copper salt:

$$Cu^{++}, SO_4^{--} + 2\,Na^+, OH^- \longrightarrow Cu(OH)_2 \downarrow + Na^+_2, SO_4^{--}$$

There are some six or seven soluble hydroxides, among them calcium hydroxide, $Ca(OH)_2$. Now lime, CaO, is easy to get by heating limestone ($CaCO_3$), and, very fortunately, it combines directly with water at ordinary temperatures to make calcium hydroxide:

$$CaO + H_2O \longrightarrow Ca^{++}, (OH^-)_2$$

With this we can get solutions of sodium hydroxide (and other soluble hydroxides) by treating a solution of sodium carbonate with calcium hydroxide:

$$Na^+{}_2, CO_3{}^{--} + Ca^{++}, (OH^-)_2 \longrightarrow CaCO_3\downarrow + 2\ Na^+, OH^-$$

The preparation of salts. As we have seen, there is a great number of salts, and they have a wide range of properties. Some are soluble and some are not; some decompose easily and some are very stable; many are colorless, but others have brilliant colors. There are many ways to make these salts, but only a few need be mentioned.

Preparation of a soluble salt. If a given salt is soluble in water, it can nearly always be made by the action of the proper acid on the right metal or its oxide, its hydroxide, or its carbonate. We have had many examples of these reactions:

$$\begin{gathered}Zn + H^+{}_2, SO_4{}^{--} \longrightarrow Zn^{++}, SO_4{}^{--} + H_2\uparrow\\ Cu^{++}, O^{--} + H^+{}_2, SO_4{}^{--} \longrightarrow Cu^{++}, SO_4{}^{--} + H_2O\\ Na^+, OH^- + H^+, NO_3{}^- \longrightarrow Na^+, NO_3{}^- + H_2O\\ Ca^{++}, CO_3{}^{--} + 2\ H^+, Cl^- \longrightarrow Ca^{++}, Cl^-{}_2 + H_2O + CO_2\uparrow\end{gathered}$$

In each case the soluble salt is crystallized by evaporating the resulting solution.

The preparation of insoluble salts. We have seen that many hydroxides are insoluble in water (p. 241) and so can be made by precipitation. Many salts are also insoluble and can be made in a similar way. It is only necessary to bring together two soluble salts, one of which gives the desired cation and the other the necessary anion of the insoluble salt.

For example, suppose we know that silver chloride ($AgCl$) is insoluble in water. We can supply silver ions by making a solution of the soluble silver nitrate ($AgNO_3$). We can get chlorine ions in a solution of sodium chloride. If we mix the two solutions, we may confidently expect silver chloride to be precipitated:

$$Ag^+, NO_3^- + Na^+, Cl^- \longrightarrow AgCl\downarrow + Na^+, NO_3^-$$

If we further know that silver chloride is *insoluble in acids*, as well as in water, we could use hydrochloric acid instead of sodium chloride:

$$Ag^+, NO_3^- + H^+, Cl^- \longrightarrow AgCl\downarrow + H^+, NO_3^-$$

In the same way we can precipitate barium sulfate ($BaSO_4$) because this salt is insoluble in both water and acids:

$$Ba^{++}, Cl^-{}_2 + H^+{}_2, SO_4^{--} \longrightarrow BaSO_4\downarrow + 2\,H^+, Cl^-$$

Importance of solubilities. It will be seen that the chemist must know a good deal about the solubility of acids, bases, and salts. There are large dictionaries or tables of solubilities to which he can turn for information. The Table of Solubilities in Appendix D will be helpful. But there are some simple rules, easy to learn, that he always keeps in mind.

Some rules of solubilities. These rules apply to all the common compounds with which the chemist is likely to work.

1. *Hydroxides:* All *hydroxides are insoluble*, except those of ammonium, sodium, potassium, calcium, barium, and strontium.
2. *Nitrates:* All *nitrates are soluble.*
3. *Chlorides:* All *chlorides are soluble*, except silver and mercurous chlorides. Lead chloride is soluble in *hot* water, not in cold.
4. *Sulfates:* All *sulfates are soluble*, except those of barium, strontium, and lead. (Sulfates of calcium and silver are only slightly soluble.)
5. *Sulfides:* All *sulfides are insoluble*, except those of ammonium, sodium, and potassium. The sulfides of calcium, barium, strontium, and magnesium are really insoluble in water, but they are changed by water into acid sulfides, which are soluble; so they cannot be made by precipitation.
6. *Carbonates, phosphates, silicates:* All *normal carbonates, phosphates, and silicates are insoluble*, except those of ammonium, sodium, and potassium.

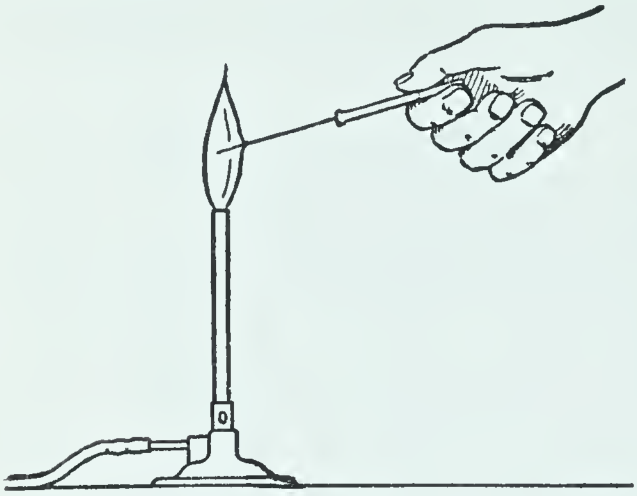


FIG. 384. Making a flame test

Chemical analysis. The chemist uses his knowledge of the solubilities of salts in still another way. Suppose he wants to know whether a bottle marked *barium chloride* actually contains this salt. He can make no good test for the salt itself, but he knows good tests for its two ions Ba^{++} and Cl^{-} *separately.* He knows that the Ba^{++} ion makes an insoluble precipitate with the SO_4^{--} ion, even in *acid* solution, and that few other ions will do this. So he dissolves in cold water a small sample of the substance to be tested and adds a few drops of sulfuric acid. If the solution contains any barium ions, he will get a white precipitate of barium sulfate ($BaSO_4$). He has now solved half his problem: either Ba^{++} ions or Pb^{++} ions are there.

He knows that silver ions form with chlorine ions a white curdy precipitate insoluble in acids. So he adds a solution of silver nitrate to a second sample of his solution:

$$2\,Ag^{+}, NO_3^{-} + Ba^{++}, Cl^{-}{}_2 \longrightarrow 2\,Ag^{+}, Cl^{-}\downarrow + Ba^{++}, (NO_3^{-})_2$$

The white curdy precipitate shows the presence of chlorine ions; so he has proved that his solution contains these. And he knows the cation is Ba^{++}, not Pb^{++}, since when he dissolved his sample he got no insoluble $PbCl_2$.

Hence his reagent bottle contains the ions of $BaCl_2$. In large part, chemical analysis depends on reasoning of this kind.

Flame tests for certain metal ions. For the ions of a few of the metals we can make a *flame test.* When compounds of these metals are heated in a colorless Bunsen flame, they give a strong color to the flame. A compound of sodium colors the flame yellow; one of potassium, violet; one of lithium, deep crimson; one of copper, green.

The test is made by dipping a clean, moist platinum wire into some of the powdered salt or into its saturated solution and then holding the wire in the flame as shown in Fig. 384.

CHAPTER SUMMARY IN QUESTION FORM

1. How does the number of possible compounds compare with the number of elements?

2. Give examples showing the general methods for making binary compounds.

3. How can we make an insoluble hydroxide?

4. Show by examples the general method for making (*a*) a soluble salt; (*b*) an insoluble salt.

5. How does a knowledge of the solubility of a compound help us to devise a way to make the compound?

6. The salts of what acid are all soluble?

7. The compounds of what metals are all soluble?

THOUGHT QUESTIONS

1. Suppose you wished to prepare some calcium chloride ($CaCl_2$) for drying gases. (*a*) What compounds would you need for its preparation? (*b*) Write the equation for the reaction involved in its preparation.

2. Suppose you had a white solid that you thought was sodium chloride, but were not certain. In a general way, tell how you would proceed to find out whether or not it was sodium chloride.

3. Suggest a method for making each of the following compounds: (*a*) zinc sulfate ($ZnSO_4$); (*b*) lead sulfide (PbS) · (*c*) calcium carbonate ($CaCO_3$).

4. A student dissolved 10 g of silver nitrate in water and added hydrochloric acid to the solution as long as a precipitate formed. (*a*) What was the precipitate? (*b*) Calculate its weight.

OPTIONAL EXERCISES

1. Make a list of metallic articles in your home and on your person that you think are (*a*) pure metals; (*b*) alloys; (*c*) electroplated.

2. What do you think would happen in each case if you brought together solutions of the following compounds: (*a*) silver nitrate and calcium chloride ($CaCl_2$); (*b*) lead nitrate ($Pb(NO_3)_2$) and potassium sulfate (K_2SO_4); (*c*) ammonium carbonate ($(NH_4)_2CO_3$) and calcium chloride; (*d*) sodium chloride and potassium nitrate. If solutions are available, test your conclusions, writing equations for the reactions that take place.

UNIT READINGS

Darrow. *The Story of Chemistry.* [Chapter X, "The Age of Metals," is well worth reading.]

Findlay. *Chemistry in the Service of Man.* [Chapter VIII tells of metals and their alloys.]

Foster. *The Romance of Chemistry.* [Chapter XVII treats of minerals and metals.]

Holmes. *Out of the Test Tube.* [Chapter XXXII, "Minerals and World Power," is brief and interesting.]

Read. *Our Mineral Civilization.* [A brief treatise that gives general information in regard to metals and minerals, written in a popular style.]

Slosson. *Creative Chemistry.* [Chapter XIV, "Metals, Old and New," is a general discussion of the metals, written in Slosson's popular and inimitable style.]

Tilden. *Chemical Discoveries and Inventions in the Twentieth Century.* [Chapter XVII is entitled "Metals and Some of Their Compounds."]

The World Book Encyclopedia. [Contains a brief but informative discussion of alloys.]

Unit Thirteen. The Lighter Metals and Their Many Uses

UNTIL about fifty years ago all the metals that had any great use were *heavy* metals, zinc being the lightest of them. The farther back we go in history the heavier the metals. The ancients knew only gold, silver, copper, lead, tin, and mercury. After these had been in use for centuries, men found out how to get iron (about as heavy as tin). After that they got no other metals for several thousand years.

Now this was no accident. The heavy metals named are the easiest to get. Some are found free in nature, and all of them are easy to get from their ores. And they did very well for the uses of the times. They made attractive ornaments. They made good tools; for most rough tools like hammers and axes need to be heavy. Copper pots and pans were heavy, but the women were strong. When iron was discovered, it was good enough for all purposes of peace and war.

But the modern world wants *light* metals as well as heavy ones. We live in an age of airships, airplanes, automobiles and trailers, high-speed streamline trains, various sorts of household implements that must be moved about and lifted. So modern industry has been studying the light metals with deep interest ever since the problem of producing aluminum was solved some fifty years ago.

In this unit we shall study some of these new light metals, and some of their compounds which long ago found uses.

CHAPTER XLIII

The Alkali Metals

[Rarely Seen as Metals. In Compounds Two Are Necessary for Life]

TABLE OF THE ALKALI METALS

NAME OF ELEMENT	ATOMIC NUMBER	DENSITY	MELTING POINT	ELECTRONS IN ORBITS
Lithium (Li)	3	0.53	186.0°	2, 1
Sodium (Na)	11	0.97	97.5°	2, 8, 1
Potassium (K)	19	0.86	62.3°	2, 8, 8, 1
Rubidium (Rb)	37	1.53	38.5°	2, 8, 18, 8, 1
Cesium (Cs)	55	1.90	26.0°	2, 8, 18, 18, 8, 1

Metals that have few uses as metals. In this chapter and in the next, we shall be studying a group of metals that few of us have ever seen or even heard of. The metals of these two chapters have few practical uses, except in the manufacture of a limited number of chemicals.

They all act vigorously on water and on moist air; and since nearly all metallic objects are exposed to both air and water, there can be few uses for these metals. To some extent they are used in alloys for special purposes.

The alkali metals. The alkali metals are five in number, as shown at the top of the page. They are called alkali metals because their hydroxides are very strong bases (alkalies). They are all univalent in their compounds — that is, have but one valence electron; so it is easy to write the formulas for their salts. While the metals themselves are rarely seen, life itself depends on a few of the compounds of sodium and of potassium. Lithium, rubidium, and cesium are of comparatively little importance, and no further mention will be made of them.

Review. The metals sodium and potassium, together with their hydroxides, were described in Chapter XX. These topics should be reviewed before we go forward in this chapter.

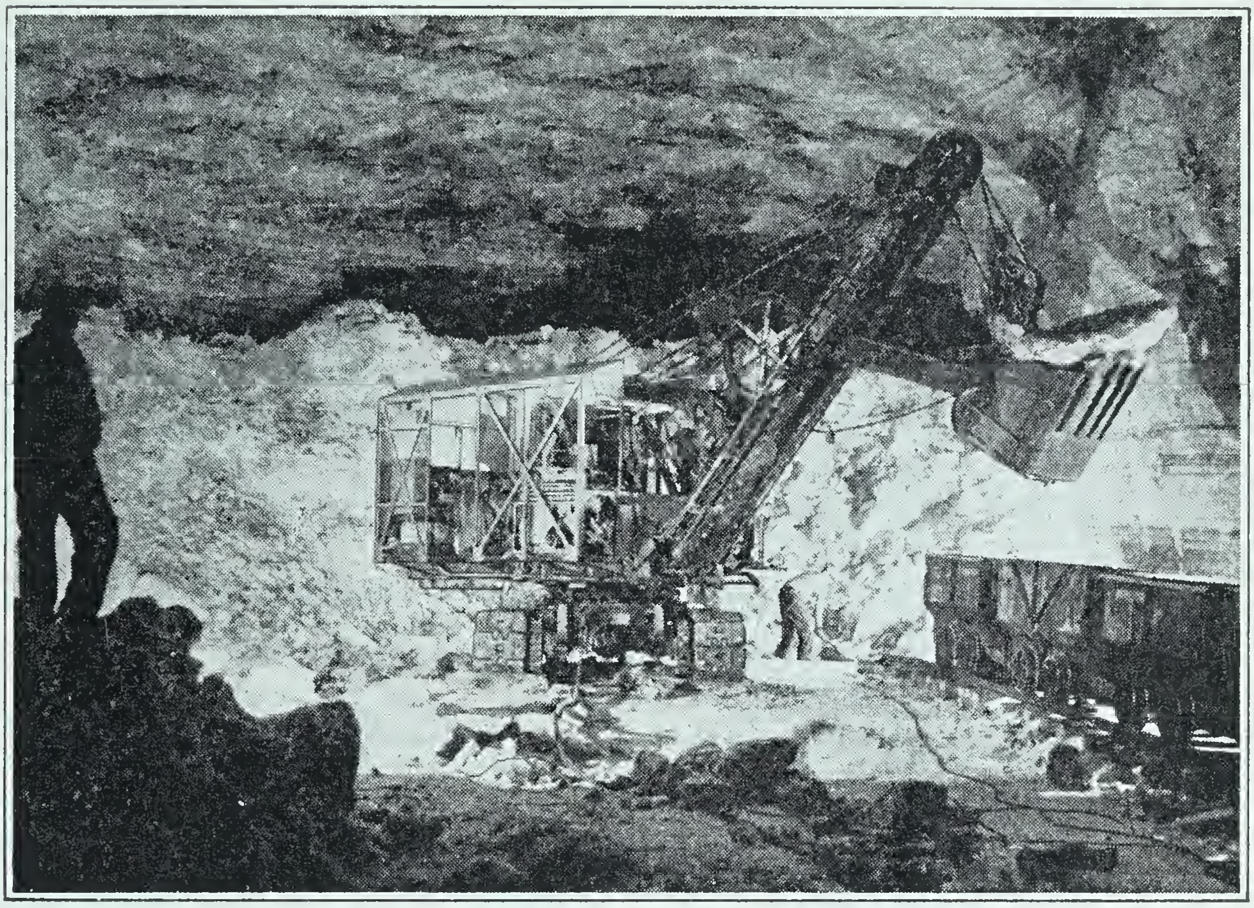


Fig. 385. View in a salt mine

Courtesy of the International Salt Co.

COMPOUNDS OF SODIUM

Sodium chloride (common salt) (NaCl). To make any other sodium compound, we always have to start with sodium chloride. So let us learn more about it. Most of us think of salt merely as seasoning for our food. This is a very important use; but it is a small one when compared with its use as the source of practically all compounds of sodium and of chlorine. These include a long list of substances of the greatest importance, such as soda, soap, glass, hydrochloric acid, chlorine, and bleaching powder.

Where we find salt. The average human body is said to keep an even balance of about 300 grams (10 ounces) of salt all the time; so we must get it from our food and drink. Nearly all natural waters of rivers, springs, and wells contain a very little salt. The oceans and a few lakes — notably Great Salt Lake (Utah) and the Dead Sea (Palestine) — are very salty. It has been estimated that if all the oceans were to be evaporated, they would give $4\frac{1}{2}$ million cubic miles of

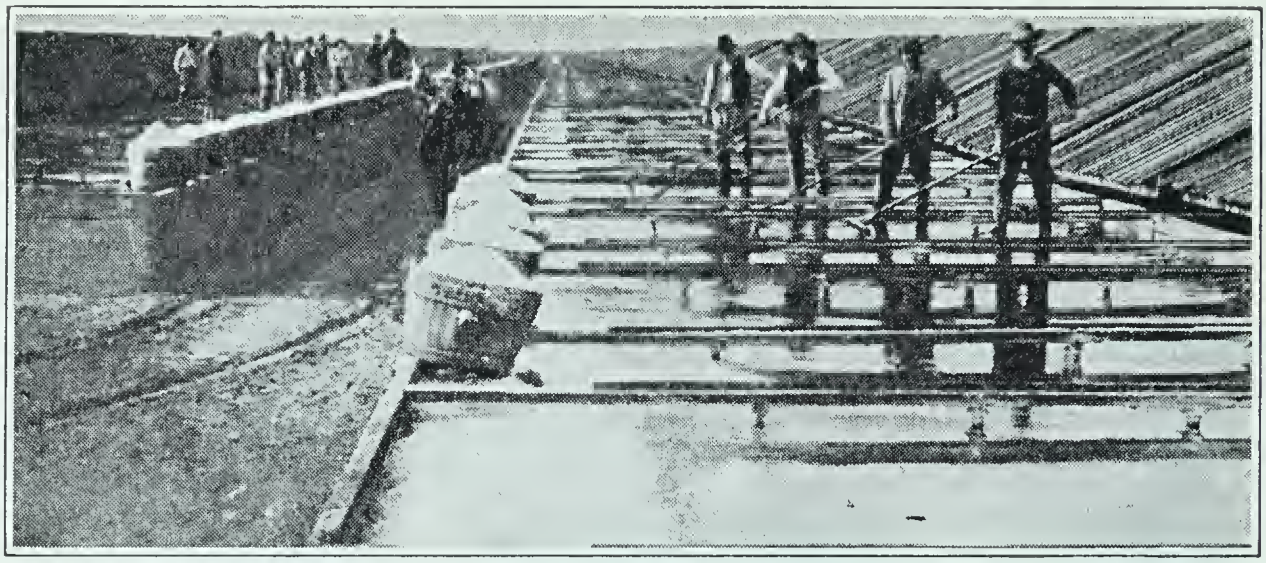


FIG. 386. Obtaining salt by evaporating sea water or salt water from deep wells

salt. This would be equal to 14½ times the bulk of all Europe above the water line.

Thick deposits of nearly pure salt are found in many places, and from these salt is mined much as coal is mined (Fig. 385). In other places wells are drilled into deep deposits, and from these a saturated salt solution (brine) is pumped. The salt is recovered from the brine either by boiling off the water or by simply running the brine into shallow basins and allowing the air and sunshine to evaporate the water (Fig. 386). In some places by the seashore, salt is recovered by evaporating sea water. In the United States most of our salt comes from New York, Michigan, Ohio, Kansas, and Louisiana.

Pure salt does not absorb moisture from the air unless the air contains a large percentage of water vapor. Cheap grades of salt often become moist even in fairly dry air, because of impurities.

The carbonates of sodium. Carbonic acid (p. 247) is a dibasic acid, and so forms two sodium salts: the normal carbonate, Na_2CO_3, and the acid salt, $NaHCO_3$. Both of these are colorless salts and are familiar household articles.

Sodium carbonate (soda ash) (Na_2CO_3). Many plants, especially those that grow in sea water, have small percentages of the sodium salts of organic acids as a part of their structure. When such plants are burned, these sodium salts are changed into sodium carbonate, which remains in the ashes. In former times sodium carbonate was made almost entirely from seaweeds in this way, and for this reason it was called *soda ash.* In ancient Egypt it was obtained from salt lakes.

The Solvay process. In the United States, sodium carbonate is made entirely by the process devised by the Belgian chemist Solvay (Fig. 387). In this process, carbon dioxide and ammonia are passed into a cold saturated solution of sodium chloride. Sodium acid carbonate, $NaHCO_3$, is then formed, as shown in the equation

$$NH_3 + CO_2 + NaCl + H_2O \longrightarrow NaHCO_3 + NH_4Cl \quad (1)$$

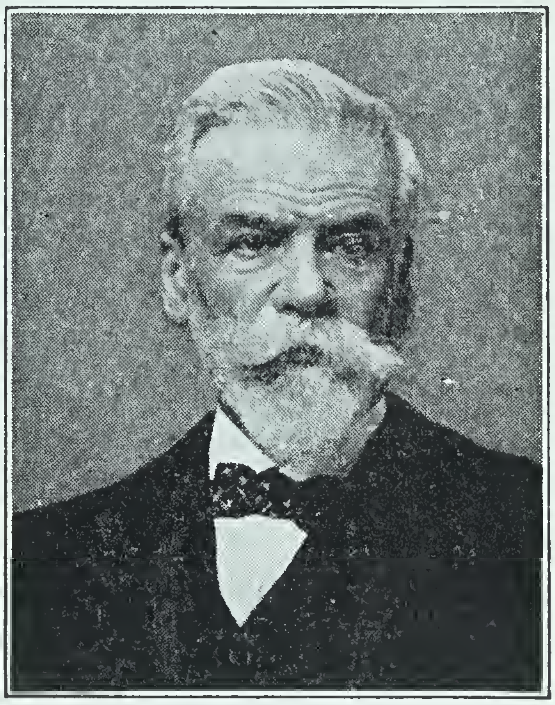


FIG. 387. Ernest Solvay (1835–1922)

A famous Belgian manufacturing chemist who developed the Solvay process for making sodium carbonate

Sodium acid carbonate is not very soluble; so most of it crystallizes from the cold solution. It is filtered off, and converted into the carbonate by heating it:

$$2\ NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2\uparrow \qquad (2)$$

All the ammonia used is recovered by heating the ammonium chloride in equation (1) with slaked lime (p. 289) and is used over again. The carbon dioxide set free in equation (2) is also used again, together with a new supply. So, after the process is in operation, the only additional materials needed to carry it on are sodium chloride, carbon dioxide, lime, and water, all of which are very cheap. It is a very ingenious process; for all the by-products are used again in making the main product, save only the calcium chloride.

Importance of sodium carbonate. Very large quantities of soda ash are used in making glass, water glass, and some kinds of soap, and in the manufacture of a great number of chemicals. It is used whenever a mild alkali is needed.

When soda ash is crystallized from water, it forms large crystals of the formula $Na_2CO_3 \cdot 10\ H_2O$, and this hydrate is called *washing soda* or *sal soda.* Its solution has a mild alkaline reaction, and it is used for laundry purposes. It is one of the few soluble carbonates.

Sodium acid carbonate ($NaHCO_3$). This compound is called sodium hydrogen carbonate, sodium bicarbonate, and baking soda. It is a necessary part of all baking powders, and is used in the kitchen in making such foods as biscuits and cakes. It is made by the Solvay process, as explained above (p. 521), and also by passing carbon dioxide into a saturated solution of soda ash:

$$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2\ NaHCO_3$$

Other compounds of sodium. Among other important compounds of sodium should be mentioned the following: *Sodium nitrate* (p. 299); *borax* (p. 396); *water glass* (p. 394); *sodium sulfate* (p. 367). *Sodium thiosulfate,* $Na_2S_2O_3 \cdot 5\ H_2O$, whose common name is *sodium hyposulfite* or merely *hypo,* is used in photography. *Sodium peroxide,* Na_2O_2, is made by burning sodium in air or oxygen, and is used as a powerful oxidizing agent. It is sometimes called *oxone.*

Hydrolysis of salts. In the study of neutralization (p. 258) we learned that when an acid and a base are brought together in solution in equivalent quantities, the hydroxyl ions of the base and the hydrogen ions of the acid unite to form water, leaving the ions of the salt in a neutral solution. From this it might be supposed that solutions of all salts in water are neutral to indicators.

This is true *if both acid and base from which the salt is formed are strong ones.* If either is very weak, the water acts upon the ions of the salt and to a slight extent reverses the act of neutralization. For example, in the case of sodium carbonate we have a slight reaction which quickly reaches equilibrium as follows:

$$Na^+, Na^+, CO_3^{--} + 2H^+\ OH^- \rightleftarrows Na^+, \overline{H^+CO_3^{--}} + Na^+, OH^-$$

This action of water on the ions of a salt to form the ions of a base and an acid is called hydrolysis. Since the hydrogen of the ion $\overline{H^+CO_3^{--}}$ is part of the weak acid H_2CO_3, it is little

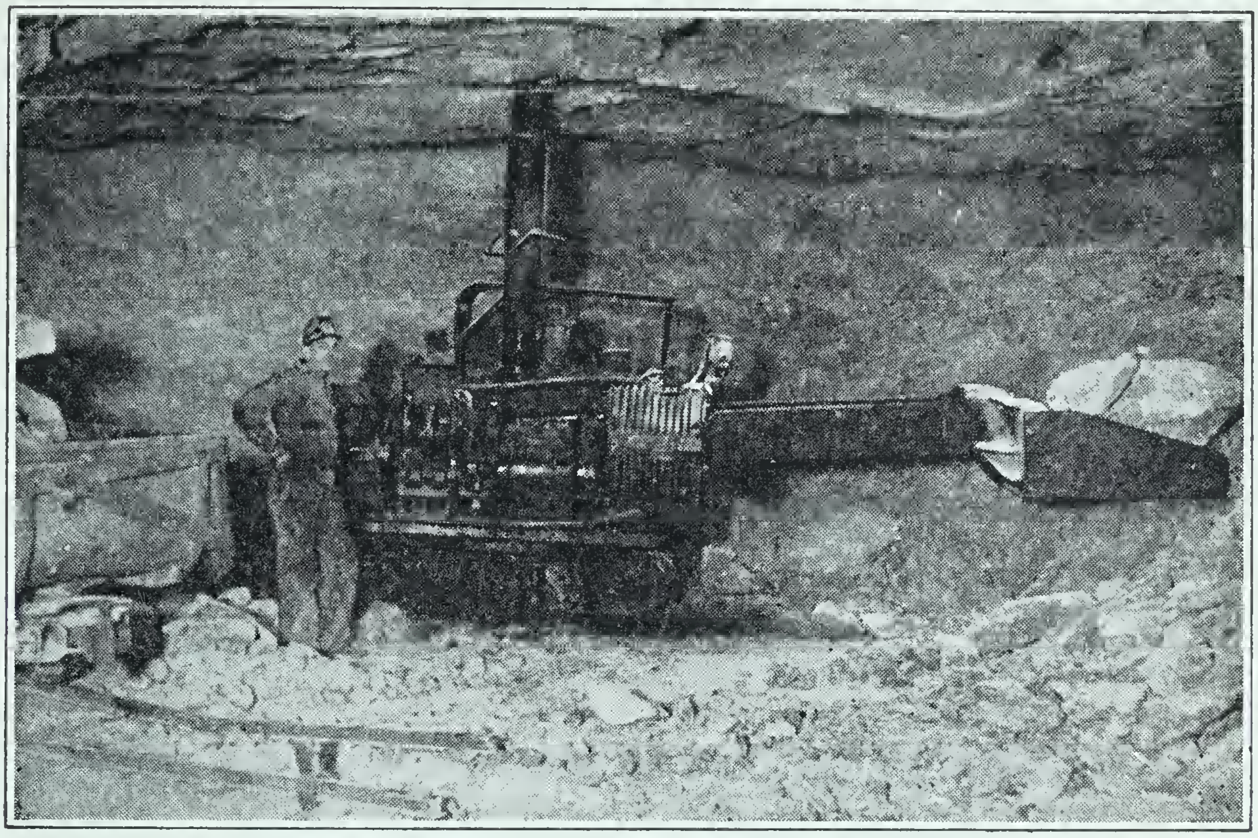


Fig. 388. Mining potassium salts in New Mexico

Courtesy of the United States Potash Company

ionized, while the OH^- ion formed is *strongly basic.* Consequently the resulting solution is *alkaline* in reaction. For the same reason, soap is alkaline toward litmus. In general the water solutions of all sodium and potassium salts of *weak acids* are alkaline in reaction.

For a similar reason the water solutions of *all salts of a weak base with a strong acid are acid in reaction.* For example:

$$Cu^{++}SO_4^{--} + 2\,H^+OH^- \rightleftarrows \overline{Cu^{++}(OH^-)_2} + H^+{}_2,\ SO_4^{--}$$

COMPOUNDS OF POTASSIUM

Occurrence. By reference to page 29 it will be seen that sodium and potassium are about equally abundant in the earth's crust. Potassium forms a part of many igneous rocks, such as the feldspars and micas. Very large deposits of the chloride and the sulfate, along with compounds of calcium and magnesium, are found at Stassfurt, Germany (*Stassfurt salts*), and in Alsace, France. Large deposits also occur in New Mexico and Texas (Fig. 388).

It is from these sources that we get the potassium necessary for fertilizers and other purposes.

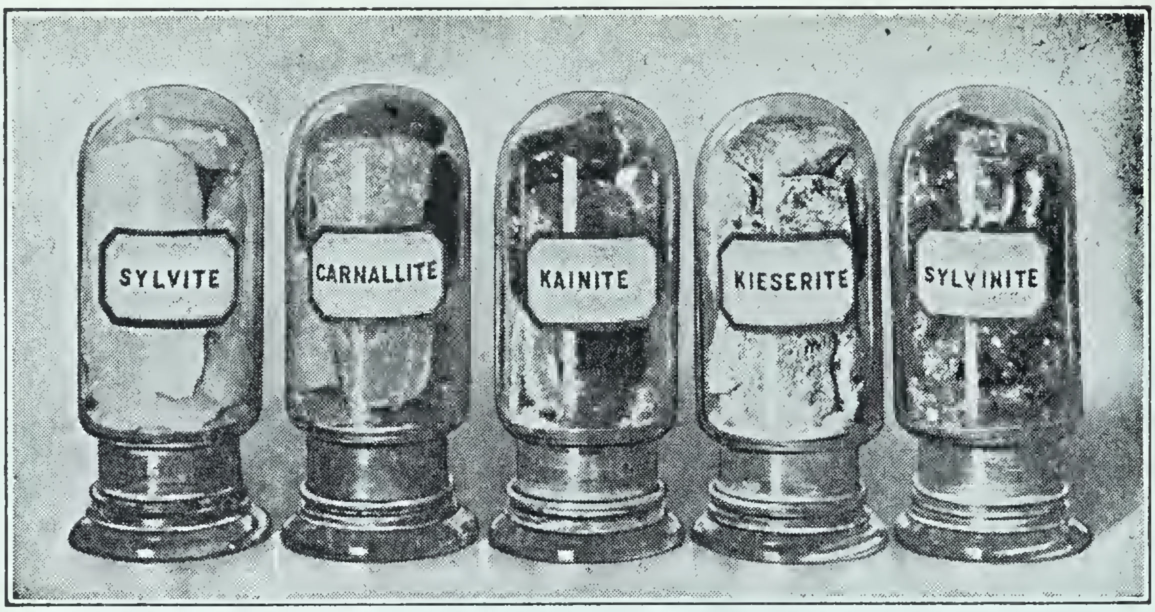


FIG. 389. The most important of the minerals constituting the Stassfurt salts

These salt deposits are made up of definite minerals (Fig. 389); some of the most important of them are these:

Sylvite . . .	KCl	Kainite . .	$KCl \cdot MgSO_4 \cdot 3\,H_2O$
Carnallite . .	$KCl \cdot MgCl_2 \cdot 6\,H_2O$	Kieserite . .	$MgSO_4 \cdot H_2O$

What potassium compounds are like. The compounds of potassium resemble the corresponding compounds of sodium so closely that for many purposes, other than as fertilizers (p. 386) and medicines, the one can be used in place of the other. Potassium compounds are made in the same general way as are sodium compounds.

Why use potassium salts at all? Except as fertilizers, why are potassium salts ever used? There are sometimes special reasons.

In medicine the two classes of salts behave differently. Potassium salts are much less soluble than sodium salts and are easier to purify. This is the reason that potassium chlorate has been used so long rather than sodium chlorate. Some sodium salts are deliquescent, as is true of sodium nitrate. So potassium nitrate is used in fine grades of gunpowder, rather than sodium nitrate.

Other compounds of potassium. Some other familiar compounds of potassium are these: *potassium hydroxide*, KOH (p. 237); *potassium chlorate*, $KClO_3$ (p. 342); *potassium nitrate*, KNO_3 (p. 300). *Potassium chloride*, KCl, and *potassium sulfate*, K_2SO_4, are used in crude form as fertilizers.

Potassium iodide, KI, and *potassium bromide*, KBr, are used in making photographic plates and films, and in medicine. *Potassium carbonate*, K_2CO_3, is used in making hard glass. All these compounds are white crystalline solids, soluble in water.

Flame tests for the alkali metals. Lithium, rubidium, and cesium are very similar to sodium and potassium, but are very rare elements. It is interesting that all five of these elements respond strongly to flame tests (Fig. 384). Compounds of lithium and rubidium color a flame different shades of red; sodium, yellow; potassium, lilac-violet; cesium, blue. Viewed in the spectroscope, each of these colored flames shows bright lines of the color of the flame, as well as some other colors. (See colored plate opposite page 273.)

CHAPTER SUMMARY IN QUESTION FORM

1. (*a*) Can a metal be an alkali? (*b*) Why is the name *alkali metals* given to the metals included in this chapter?

2. Which are the more important commercially, the alkali metals or their compounds?

3. Prepare a table giving information on five compounds of sodium, under the following heads:

Chemical Name	Formula	Common Name (if Any)

4. (*a*) Why is sodium chloride of so much importance? (*b*) State some of its uses.

5. State how many sodium salts of each of the following acids are known: (*a*) carbonic acid; (*b*) nitric acid; (*c*) sulfuric acid; (*d*) phosphoric acid (p. 375).

6. Give the names and formulas of each of the salts referred to in the preceding question.

7. (*a*) Is it reasonable to predict that each of the alkali metals will form the same number of salts as sodium, and that these will be similar in character? (*b*) Give the reasons for your answer.

8. Give the common names of each of the compounds represented by the following formulas, and give a reason why each name is appropriate: (*a*) NaCl; (*b*) $NaHCO_3$; (*c*) Na_2CO_3; (*d*) $NaNO_3$.

9. Study the equations on page 521 for the preparation of sodium carbonate, and answer the following questions regarding them: (*a*) Why is salt used? (*b*) Why is carbon dioxide used? (*c*) What property has sodium bicarbonate that makes it possible to separate it? (*d*) What use is made of the by-product carbon dioxide? (*e*) How can we obtain ammonia from the by-product ammonium chloride, so as to use it again?

10. Rearrange the names of the compounds in column *A*, below, so that each one will stand opposite the most closely associated term in column *B*.

A	*B*
Sodium thiosulfate (hypo)	Fertilizers
Sal soda	Manufacture of glass
Soda ash	Laundry purposes
Caustic soda	Baking
Sodium nitrate	Soap
Sodium bicarbonate	Food condiment
Sodium chloride	Photography

11. Complete each of the following equations if hydrolysis occurs:

$$NaCl + H_2O \longrightarrow$$
$$Na_2CO_3 + H_2O \longrightarrow$$
$$CuSO_4 + 2\,H_2O \longrightarrow$$

12. (*a*) What is the principal use of potassium compounds? (*b*) Where is the chief source of these compounds?

13. For what purpose is potassium nitrate better adapted than sodium nitrate?

14. State what ions are present in water solutions of each of the following compounds: (*a*) sodium hydroxide; (*b*) sodium carbonate; (*c*) sodium sulfate.

15. In the preceding question, what one ion is common to all the solutions?

THOUGHT QUESTIONS

1. (*a*) Write the formulas for each of the carbonates of sodium. (*b*) How could you prepare carbon dioxide from each of these? (*c*) If you had equal weights of each, which would give you the most carbon dioxide?

2. What are the products formed by passing a current of electricity through a water solution of (*a*) potassium chloride? (*b*) potassium sulfate?

3. In former times the farmers made much of their soap by boiling waste fats with the liquid obtained by pouring water on wood ashes. (These contain potassium carbonate.) (*a*) Explain why soap can be made in this way. (*b*) Would the soap so formed be hard or soft (p. 483)?

4. In the preparation of what compound already studied is sodium sulfate a by-product?

5. (*a*) Study the formula of borax (p. 396) and state whether this compound is an acid, a base, or a salt. (*b*) What effect do you think a water solution of borax would have on blue litmus and on red litmus?

6. A solution of sodium chloride has no effect on either blue or red litmus, while sodium carbonate turns red litmus blue. Explain.

7. 1 kg of sal soda contains what weight of water of hydration?

OPTIONAL EXERCISES

1. Suppose you had an abundant supply of sodium chloride. Tell how you could prepare each of the following substances from it, writing the equations for all the reactions involved: (*a*) sodium sulfate; (*b*) sodium carbonate; (*c*) sodium bicarbonate; (*d*) sodium hydroxide; (*e*) hydrochloric acid; (*f*) sodium; (*g*) chlorine; (*h*) potassium chlorate.

2. Suppose that a soda-acid fire extinguisher (p. 152) is charged with 4000 g of sodium bicarbonate and with sufficient sulfuric acid to react with it completely. Calculate the volume of the carbon dioxide that would be evolved.

CHAPTER XLIV

Calcium and Its Relatives

[The Builders' Friend through the Ages]

TABLE OF THE FAMILY

NAME OF ELEMENT	ATOMIC NUMBER	DENSITY	MELTING POINT	ELECTRONS IN ORBITS
Calcium (Ca)	20	1.55	810°	2, 8, 8, 2
Strontium (Sr) . . .	38	2.6	800° (?)	2, 8, 18, 8, 2
Barium (Ba)	56	3.5	850°	2, 8, 18, 18, 8, 2
Radium (Ra)	88	—	—	2, 8, 18, 32, 18, 8, 2

CALCIUM AND ITS COMPOUNDS

We have long used compounds of calcium. In early times men lived in huts made of sun-dried clay bricks held together by a plaster of mud. One of the first steps ahead was to use stone in place of brick, and a lime mortar instead of mud. The stones were very often limestone. The kings of Nineveh and Babylon lined the walls of their palace rooms and halls with lovely sculptures of alabaster. As time went on, the builders added to their materials marble, stucco, plaster, plaster of Paris, cement, and glass.

All these materials are compounds of calcium. The skeletons that are the framework of all animals are largely made of calcium phosphate. So compounds of calcium are good friends of both builders themselves and of the structures they make.

Each of the four metals of this family has two electrons in its valence orbit and is bivalent in nearly all its compounds.

Pure calcium. The metal calcium, like sodium (p. 233), can be made by the electrolysis of its melted chloride. It is a silvery metal, about one fifth as heavy as iron, and, like sodium, decomposes water rapidly:

$$Ca + 2\,H_2O \longrightarrow Ca(OH)_2 + H_2\uparrow$$

Because of its great affinity for oxygen it is a powerful reducing agent. It is of use in some bearing-metal alloys.

Calcium carbonate ($CaCO_3$). Enormous quantities of calcium carbonate are found in nature. *Limestone* is its most abundant form and sometimes makes up whole mountain ranges. Limestone is never pure calcium carbonate but contains variable percentages of magnesium carbonate, clay, silica, and compounds of iron. *Dolomite* is another mountain-forming mineral that is more than half calcium carbonate.

Pearls, *coral*, and various *shells* are largely calcium carbonate. *Calcite* is a very pure crystalline form, and often is found in large transparent crystals (Fig. 390) called *Iceland spar*. *Marble* is composed of very small calcite crystals.

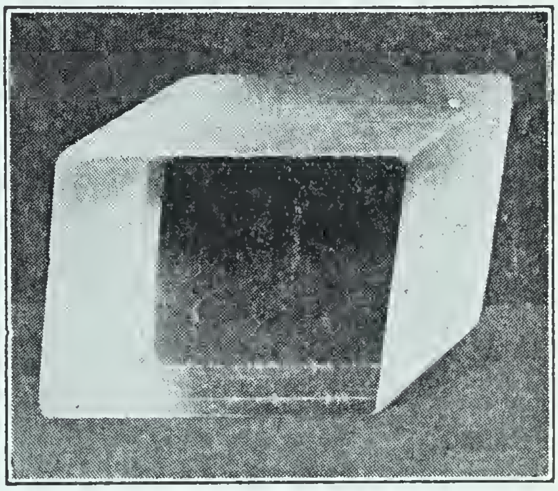


FIG. 390. A crystal of Iceland spar

In the laboratory we can get pure calcium carbonate by mixing solutions of a calcium salt and a soluble carbonate:

$$Na_2CO_3 + CaCl_2 \longrightarrow 2\,NaCl + CaCO_3\downarrow$$

When made in this way, it is a soft, white, insoluble powder often called *precipitated chalk*, and is much used as a polishing powder (tooth powder).

The natural varieties of calcium carbonate have many uses, as in making lime and carbon dioxide; in metallurgical operations, especially in making iron and steel; in the manufacture of soda and glass; for building-stone (Fig. 391); and as ballast for roads.

Calcium acid carbonate ($Ca(HCO_3)_2$). Carbonic acid has the formula H_2CO_3 (p. 247). Since calcium is bivalent, one calcium atom will displace both of the hydrogen atoms in the molecule of carbonic acid, forming the *normal* salt $CaCO_3$. How, then, is it possible to have a calcium *acid* carbonate? The answer is, by putting an atom of calcium in place of *one* atom of hydrogen *in each of two molecules* of carbonic acid. This gives us the formula

$$Ca\begin{cases} HCO_3 \\ HCO_3 \end{cases} \quad \text{or} \quad Ca(HCO_3)_2$$

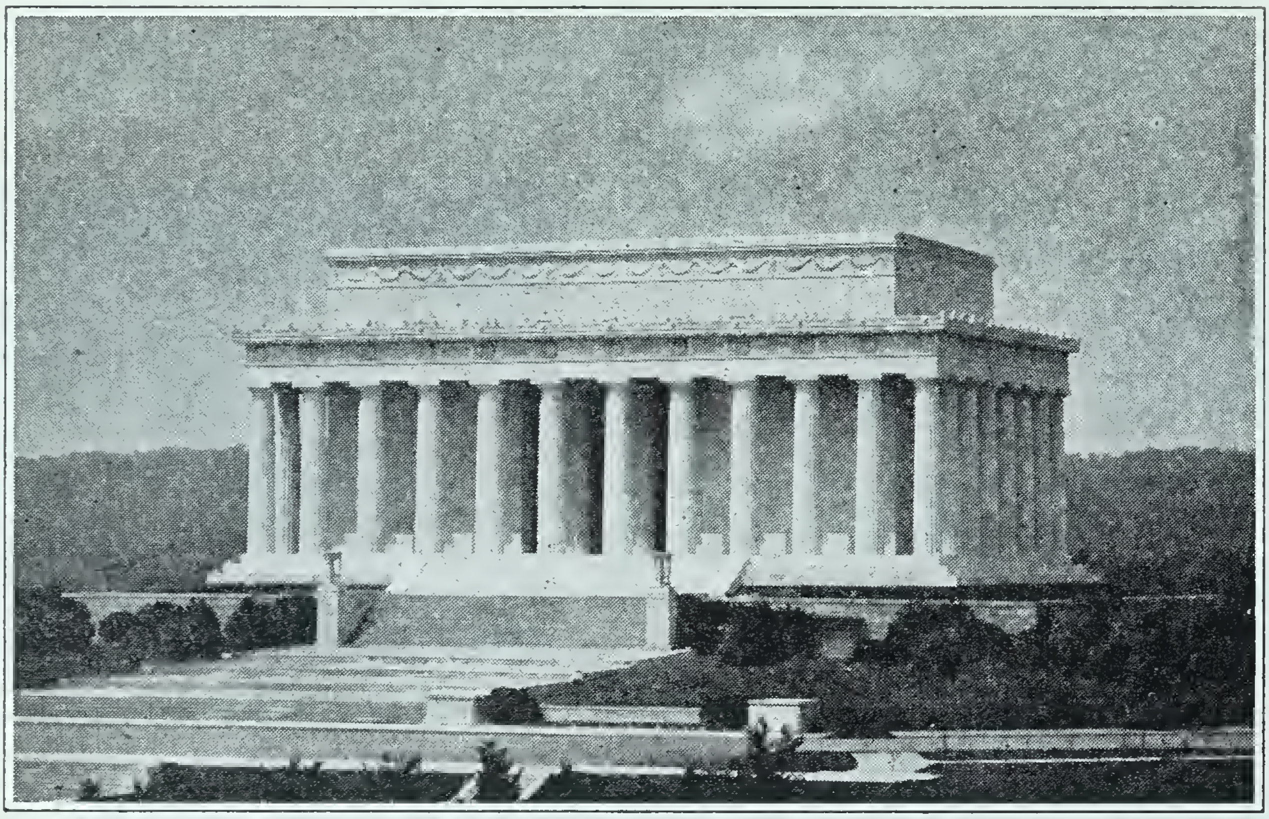


FIG. 391. The Lincoln Memorial at Washington, built of white marble and limestone

Normal calcium carbonate is insoluble in pure water; *but it readily dissolves in water containing carbonic acid.* This is because the normal carbonate reacts with carbonic acid to form the acid salt, which is very soluble:

$$CaCO_3 + H_2CO_3 \longrightarrow Ca(HCO_3)_2$$

The resulting acid carbonate exists only in cold solution. If we attempt to get it by evaporating the solution, it breaks up into carbonic acid and the normal insoluble carbonate. So the reaction shown by the above equation is a reversible one, and will go in either direction, depending on conditions.

Formation of caves. Carbon dioxide often occurs in porous rocks and underground fissures. Natural waters coming in contact with this gas dissolve large percentages of it, forming carbonic acid (p. 247). From what we have learned in the last paragraph, it is evident that such waters will readily dissolve limestone, which is chiefly calcium carbonate. This solvent action, going on through the ages, has slowly made caves. Some of these, such as the Mammoth Cave of Kentucky and the Carlsbad Caverns of New Mexico, are very large.

When water, saturated with calcium acid carbonate, drips from the roof of a cave, the water partially evaporates, and

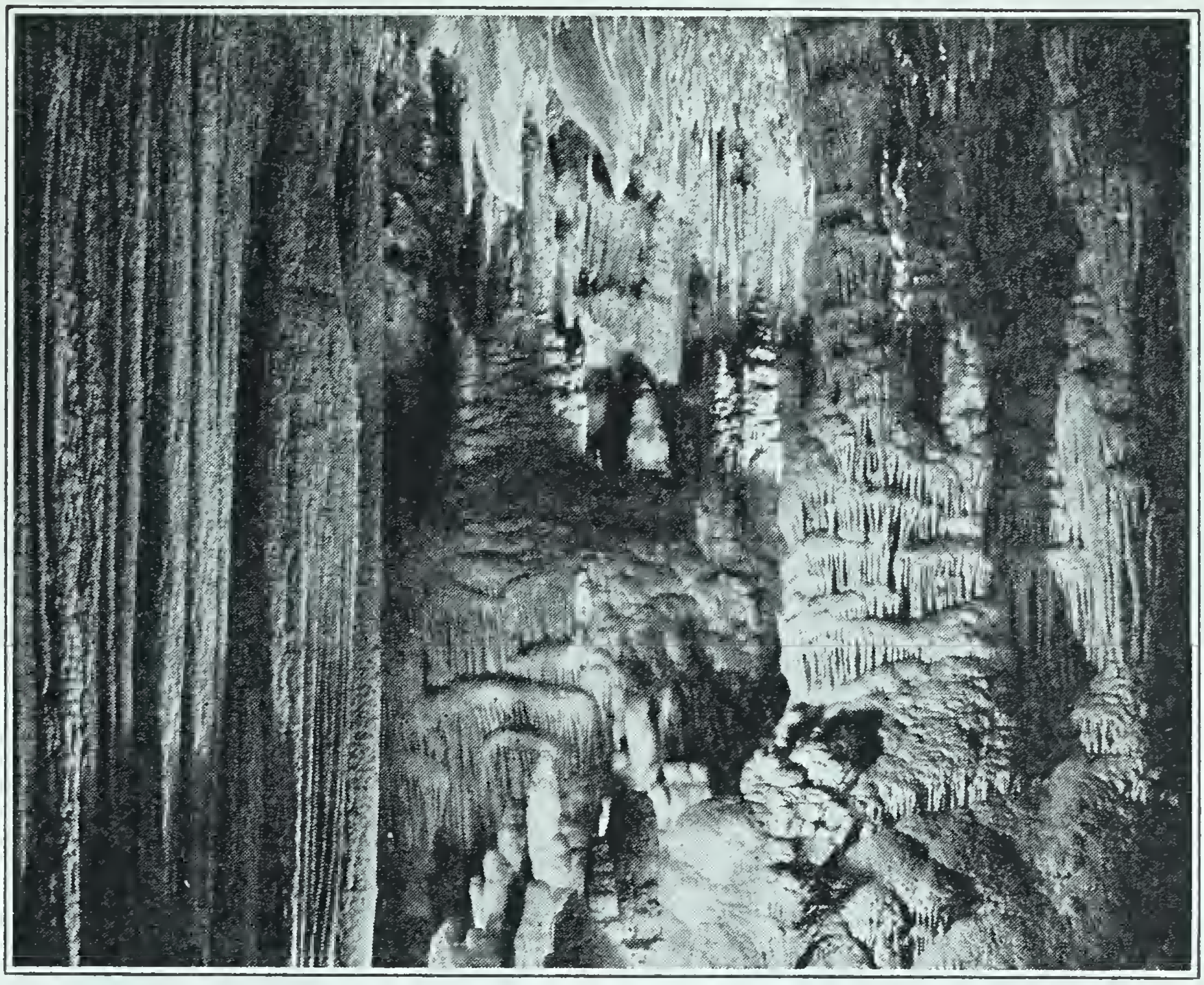


Fig. 392. Stalactites and stalagmites in the Luray Cavern, Virginia

Courtesy of the Geological Survey of Virginia

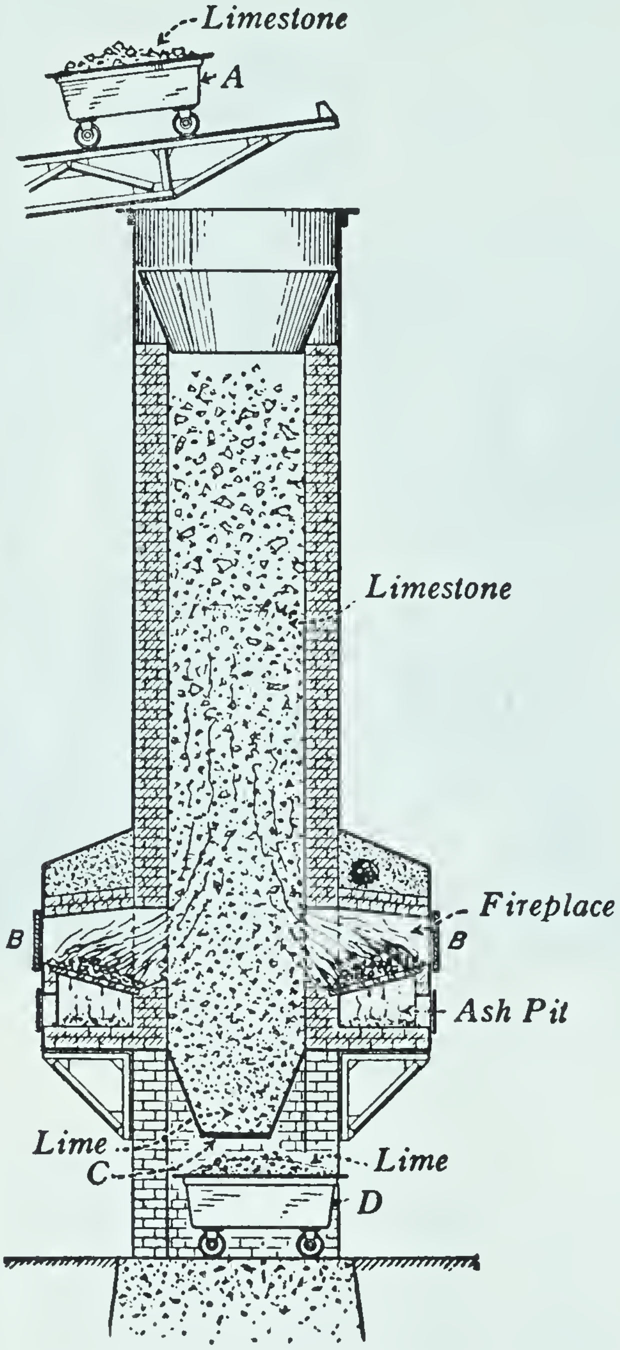
normal carbonate forms. This often grows into icicle-shaped masses called *stalactites*, hanging from the roof of the cave (Fig. 392). A similar mass of the carbonate, called a *stalagmite*, grows upward from the floor of the cave where the drip falls.

Calcium oxide (lime) (CaO). Almost everyone is familiar with *lime*, or *quicklime*, as we sometimes call it. Lime is impure calcium oxide. It is made by heating limestone in large kilns, as explained in Figs. 294, 393. If we heat pure calcium carbonate, we obtain pure calcium oxide:

$$CaCO_3 \longrightarrow CaO + CO_2\uparrow$$

When we heat limestone, the same reaction takes place; but the impurities in the limestone remain in the lime.

Lime is a white solid that melts only in the intense heat of the electric furnace. When exposed to the air, it absorbs water and also carbon dioxide, being changed into a carbonate. It is then said to be *air-slaked*. Several million tons



A modern limekiln plant consists of a number of kilns arranged in a group; a vertical section of one of the kilns is shown in the figure. Limestone is added at the top of the kiln as shown at *A*. The fire boxes *B*, *B* are built around the lower part of the kiln, and all lead into the central stack. Hot products of combustion are drawn up through the kiln, and the limestone is decomposed by the heat. Air is drawn in at the bottom (*C*) of the kiln. This serves to cool the hot lime at the base of the kiln and to furnish hot oxygen for combustion. The products of combustion and the carbon dioxide resulting from the decomposition of the limestone escape near the top of the kiln. From time to time, the lime is dropped into cars (*D*) run under the kiln

FIG. 393. A vertical section of a limekiln

of lime are produced annually in the United States, and most of it is used in making calcium hydroxide.

Calcium hydroxide (slaked lime, or hydrated lime) ($Ca(OH)_2$). Water reacts vigorously with lime, forming calcium hydroxide, much heat being given off in the reaction:

$$CaO + H_2O \longrightarrow Ca(OH)_2 + 15{,}540 \text{ cal}$$

This reaction is called *slaking* the lime. When pure, calcium hydroxide is a light, white powder. It is sparingly soluble in water, forming a strongly alkaline solution called *limewater*. Owing to its cheapness it is used in the industries

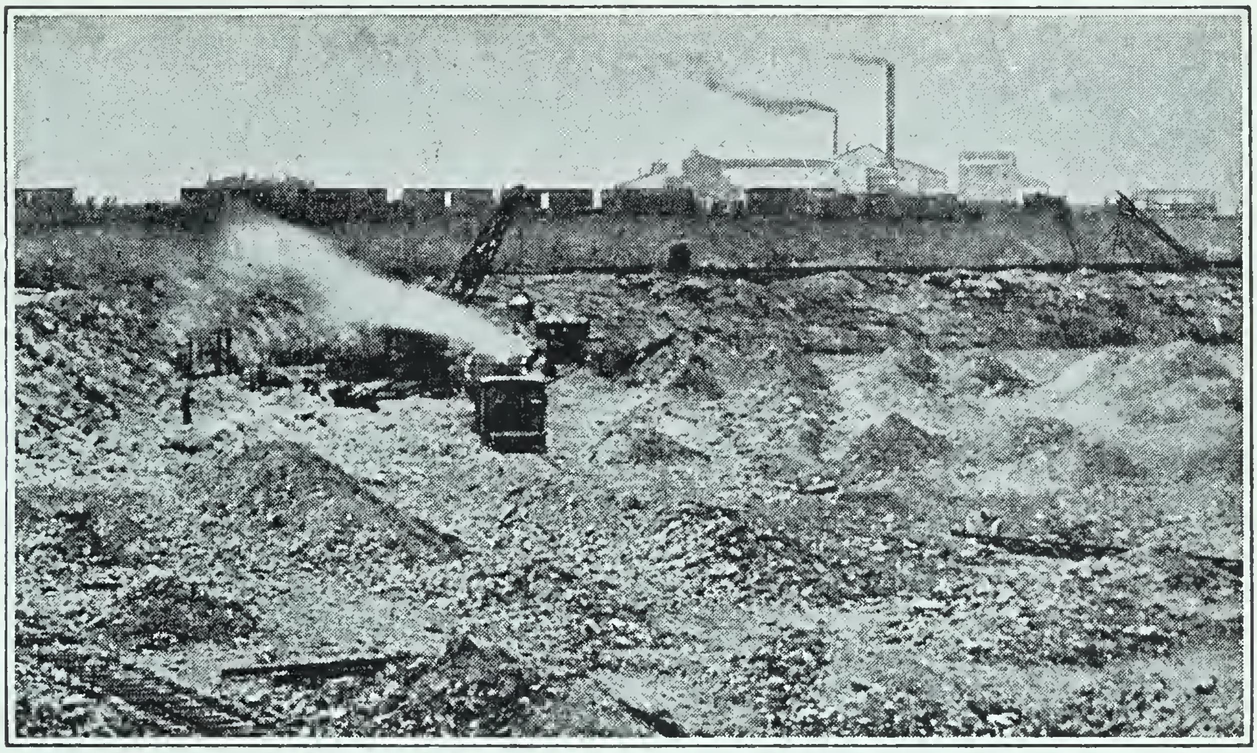


Fig. 394. A quarry of gypsum in Michigan

whenever an alkali is needed. It is used in making bleaching powder (p. 343), and the hydroxides of sodium and potassium. It is also used to remove sulfur compounds and carbon dioxide from coal gas, to remove the hair from hides in making leather, for making mortar and plaster, and for neutralizing the acids in soils.

Mortar, plaster, stucco. Ordinary mortar is made by mixing calcium hydroxide, sand, and water. When spread upon a porous surface and exposed to air, the water is rapidly lost (by evaporation and absorption), and the mortar becomes firm, or *sets*. The mortar is still further hardened by taking up carbon dioxide from the air to form calcium carbonate:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

The mortar becomes very hard and sticks firmly to the surface upon which it has been spread. The sand gives body to the mortar and prevents too much shrinkage. At present cement is usually added to the mortar mixture.

Plaster for inside walls used to be made of slaked lime and of hair or wood fibers. Now various manufactured materials are used, plaster of Paris being the chief one. Plasters for outside walls are called *stucco*. They are made of sand (or similar material) and a binder of calcium hydroxide and cement.

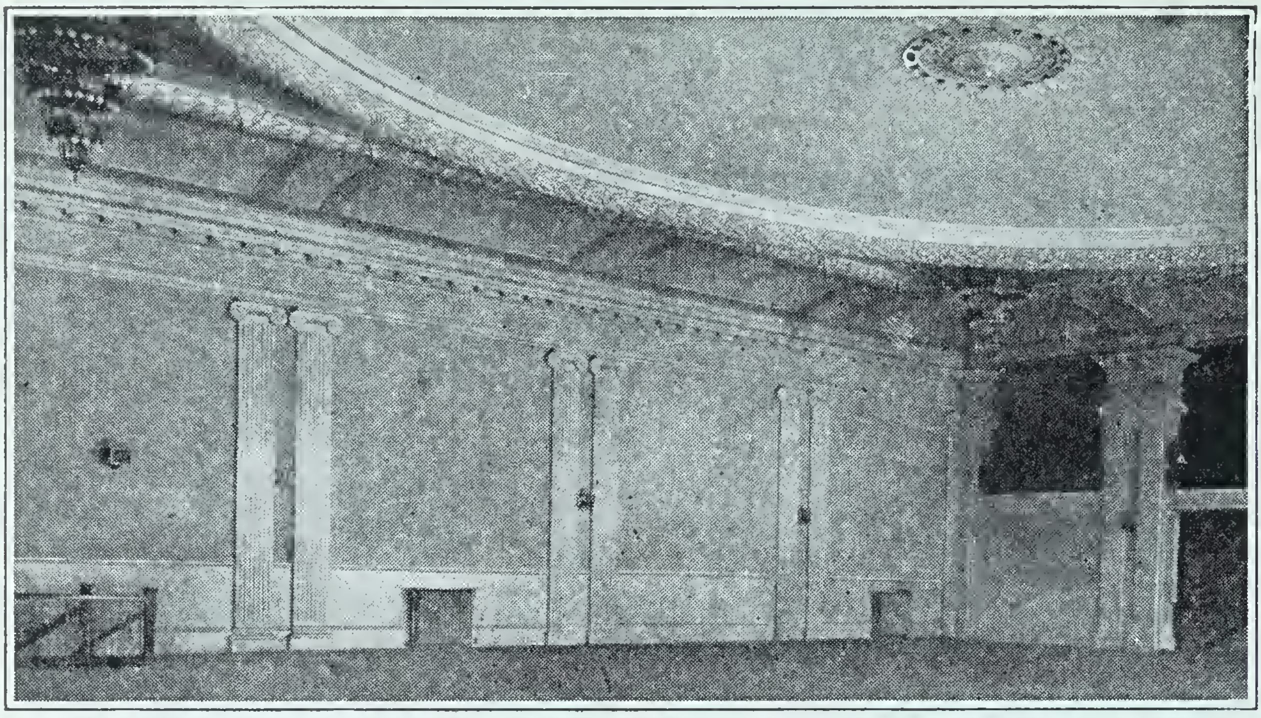


Fig. 395. The walls and ceiling of this room are finished with a plaster composed chiefly of plaster of Paris

Calcium sulfate ($CaSO_4$). Calcium sulfate is found in nature in a number of mineral varieties, the most plentiful of which is *gypsum*, $CaSO_4 \cdot 2\,H_2O$. *Alabaster* is a form of gypsum that can be quarried in large, rocklike, translucent masses and cut into slabs or artistic figures. Gypsum is quarried (Fig. 394) in very large quantities, especially in New York, Michigan, and Iowa. It is used as a material in making wallboard and shingles, as a filler in paper-making, in fertilizers, and especially in making *plaster of Paris.* It is a white solid, very slightly soluble in water.

Plaster of Paris ($(CaSO_4)_2 \cdot H_2O$). This is a fine, white powder made by carefully heating gypsum until three fourths of the water of hydration is driven off. When this powder is moistened with water, a plastic mass is formed which gradually hardens, or *sets*, as the sulfate takes up its original hydrate water. So it is valuable for molding casts, for stucco work, and for wall plaster (Fig. 395).

Calcium carbide (CaC_2). Calcium carbide is made on a large scale by heating a mixture of coke and lime in an electric furnace (Figs. 396, 397):

$$CaO + 3C \longrightarrow CaC_2 + CO\uparrow$$

It is of the greatest value to us, because it is the starting point (1) in making acetylene and so of the many organic

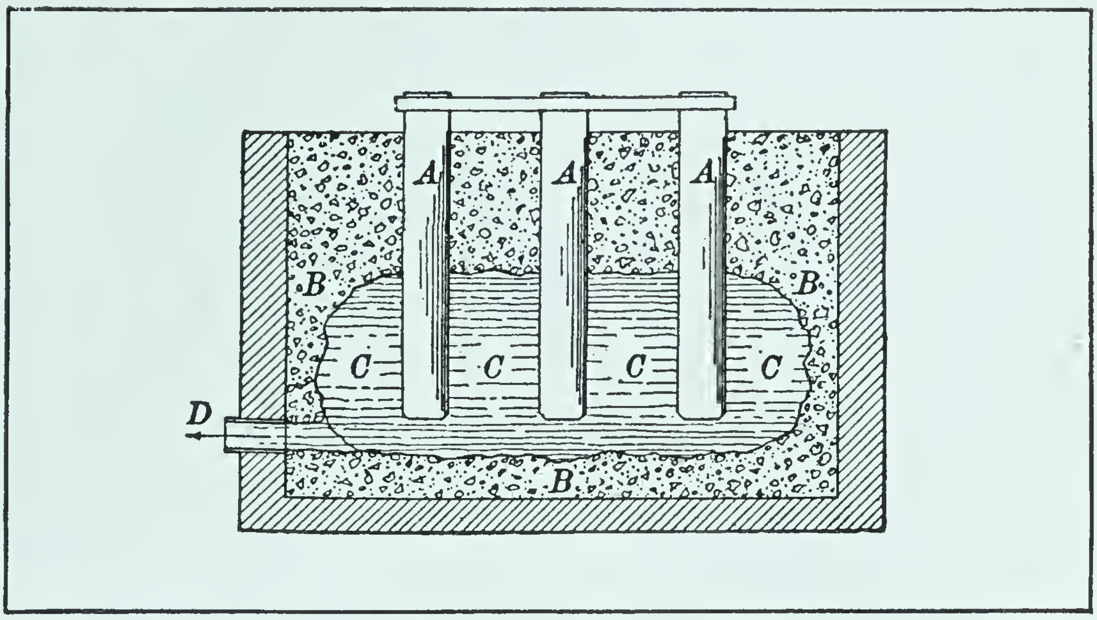


Fig. 396. A furnace for making calcium carbide

A large brick box open at the top is fitted with carbon electrodes *A*, *A*, *A*, and filled with a mixture, *B*, of lime and coke. Sufficient current is used to secure a temperature of about 2000°. The lime and coke react to form calcium carbide, *C*, which melts as fast as it forms and is drawn off from time to time at *D*

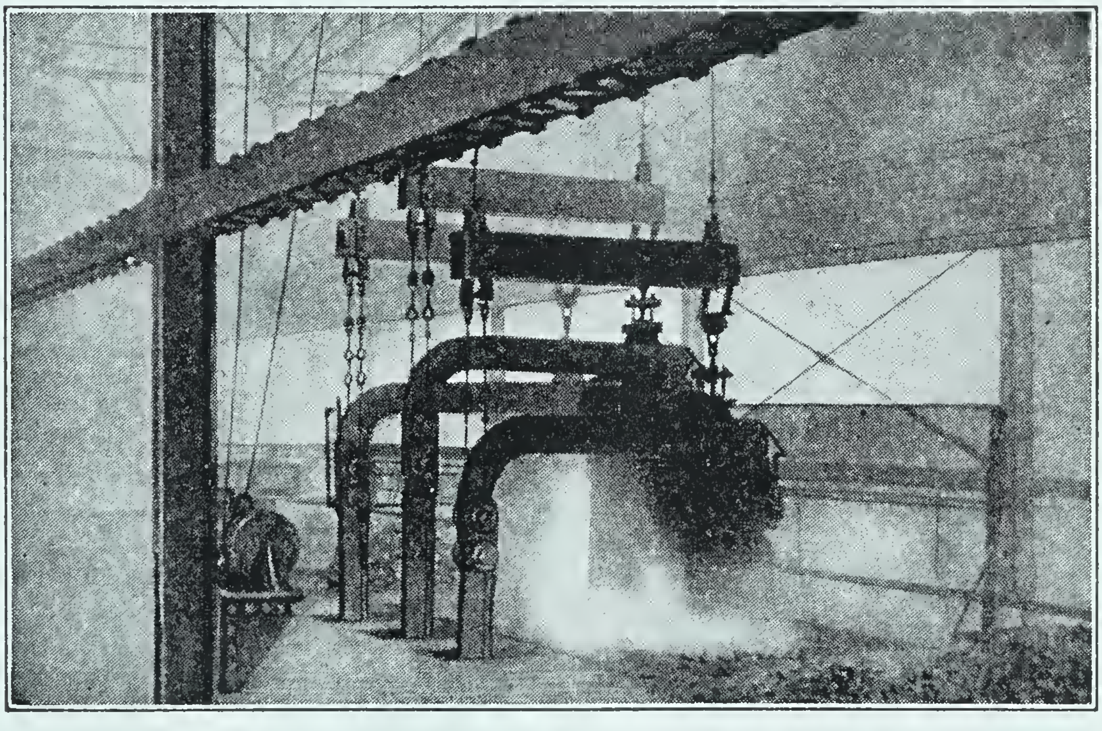


Fig. 397. View in a plant for making calcium carbide, showing the large carbon electrodes which dip into the furnace below

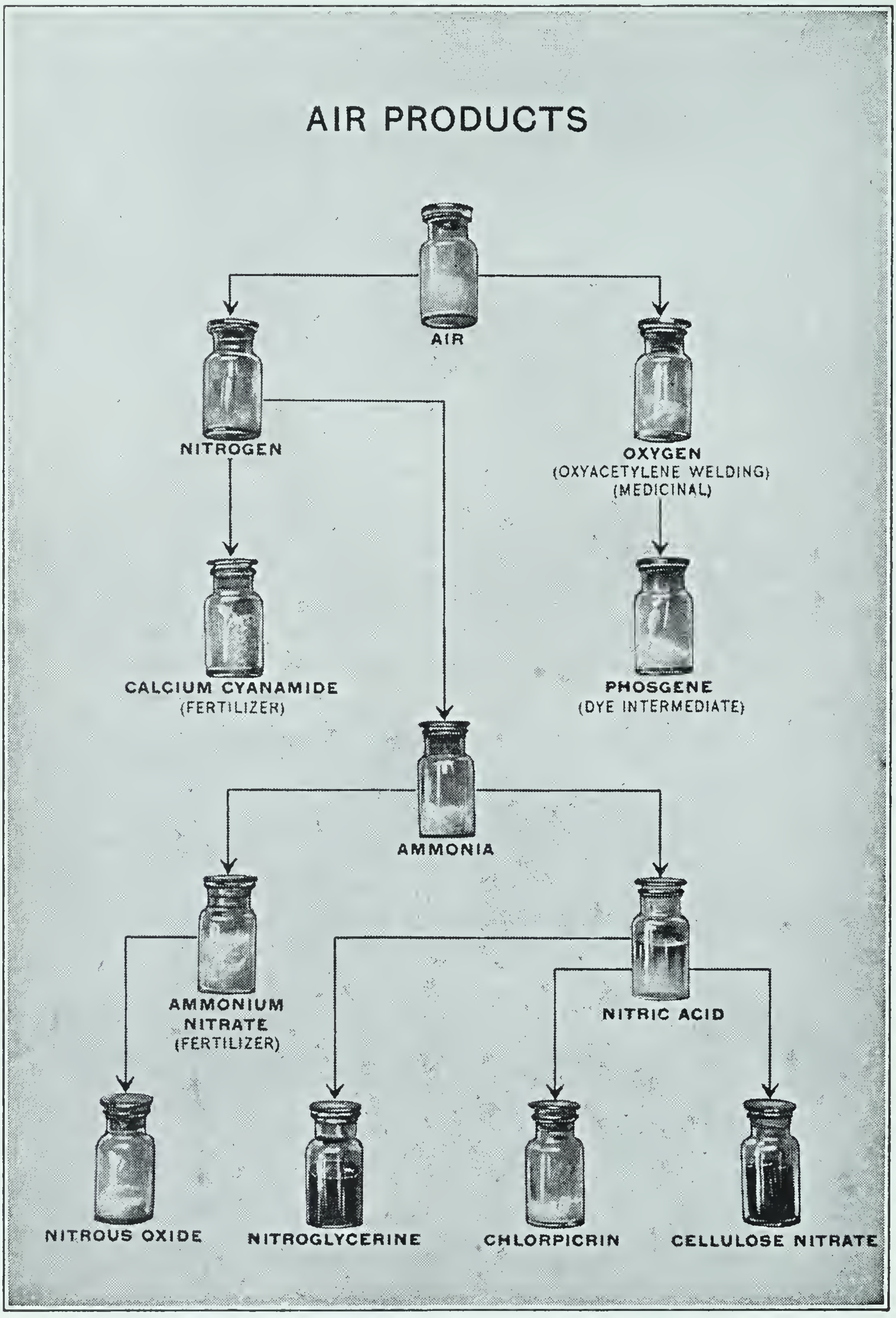

AIR PRODUCTS
AIR
NITROGEN
OXYGEN
(OXYACETYLENE WELDING)
(MEDICINAL)
CALCIUM CYANAMIDE
(FERTILIZER)
PHOSGENE
(DYE INTERMEDIATE)
AMMONIA
AMMONIUM
NITRATE
(FERTILIZER)
NITRIC ACID
NITROUS OXIDE
NITROGLYCERINE
CHLORPICRIN
CELLULOSE NITRATE

Fig. 398. Some products obtained from the air

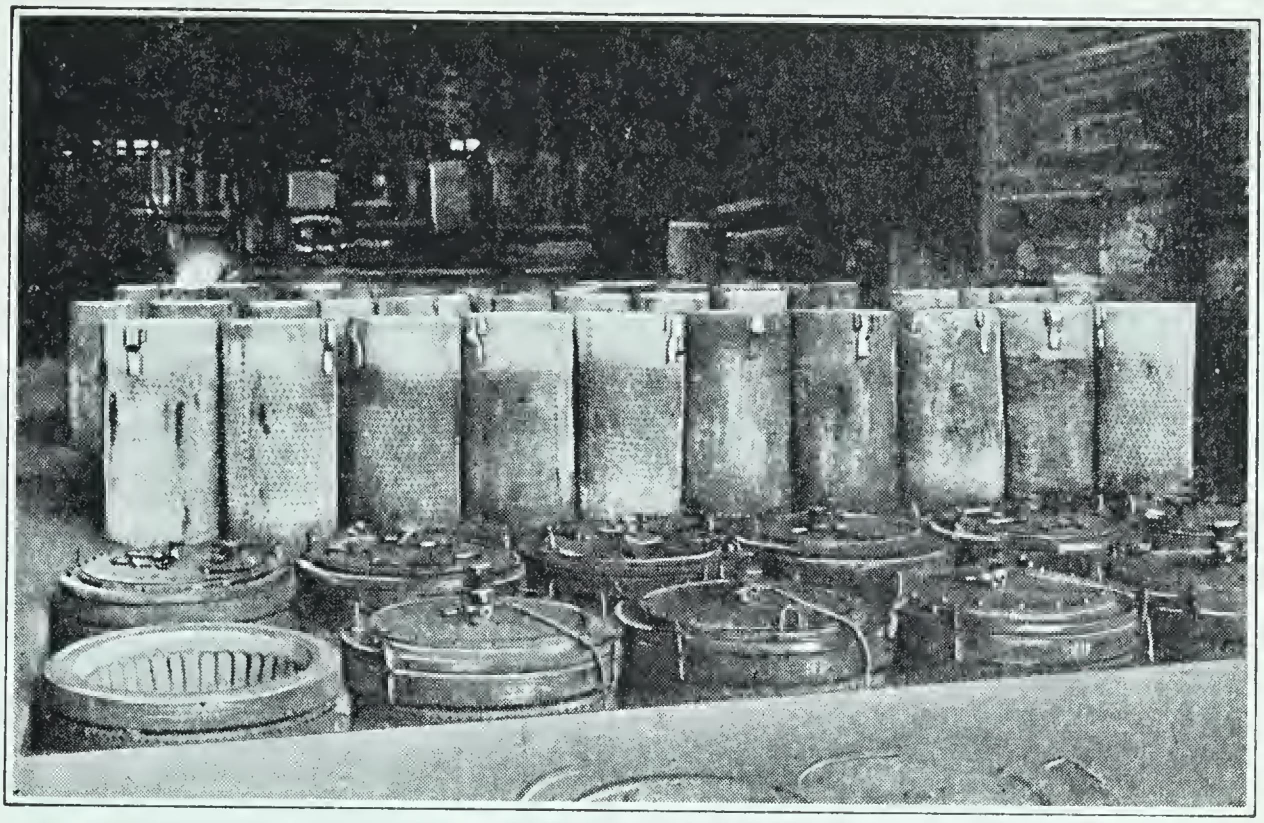


FIG. 399. View in plant for making calcium cyanamide

Calcium carbide is placed in the perforated steel cans shown in the background. These are then lowered into the furnaces shown in the foreground. The carbide is heated to about 1000°, and then pure nitrogen obtained from liquid air is passed over it, the two combining to form the cyanamide

compounds made from acetylene, and (2) in making the important nitrogen fertilizer called cyanamide.

Calcium cyanamide ($CaCN_2$). When nitrogen is passed over hot calcium carbide, the two react, forming a compound called *calcium cyanamide* (Fig. 399).

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C$$

The commercial product is impure, containing about 65 per cent of the calcium cyanamide; the impurities are lime and carbon. It is ground, moistened with water (to slake the lime present), and in dry form sold as a fertilizer under the name of *cyanamide.* Its value as a fertilizer lies in the fact that all its nitrogen is available as a plant food.

Calcium chloride ($CaCl_2$). This compound occurs in some natural waters, and is also a by-product in the Solvay process (p. 521). It attracts moisture from the air (is deliquescent), and because of this property it is being used to lay the dust on roads, tennis courts, and in dusty mines.

Calcium phosphate ($Ca_3(PO_4)_2$). We have already seen the value of this compound as a fertilizer (p. 383). It is the chief mineral constituent of bones; so *bone ash* is largely calcium phosphate. Both calcium and phosphorus must be supplied in some form to the body in food and drinking water, both for bone growth and for other functions as well.

Nitrogen fixation. Formerly the sodium nitrate deposits of Chile were the sole source of all the nitric acid of commerce and of most nitrates used as fertilizers, while our supply of ammonia came as a by-product in the manufacture of coal gas.

In recent years methods have been devised for making these compounds from the nitrogen of the air. These processes are called *nitrogen fixation.* Of these the Haber process (p. 289) is the most important, followed by the cyanamide process explained above. By far the largest part of the world's supply of ammonia, nitric acid, and its salts is now prepared from atmospheric nitrogen, and the amounts are constantly increasing.

Other compounds of calcium. *Bleaching powder,* $CaOCl_2$ (p. 343). *Calcium fluoride,* CaF_2 (fluorite); a crystalline mineral used as a flux and for making all fluorine compounds (p. 335). *Calcium nitrate,* $Ca(NO_3)_2 \cdot 4\,H_2O$; made from air nitrogen for a fertilizer. *Calcium oxalate,* CaC_2O_4, a salt of oxalic acid ($H_2 \cdot C_2O_4$); important in chemical analysis, as it is one of the most insoluble salts of calcium. *Calcium arsenate,* $Ca_3(AsO_4)_2$; used as an insecticide spray (p. 378).

STRONTIUM AND BARIUM

Strontium and barium. These two metals resemble calcium closely, but are much rarer and more difficult to prepare. Metallic barium is used to harden lead as a bearing-metal alloy. A nickel-barium alloy is used in automobile spark plugs.

Their volatile compounds give a color to a hot flame (p. 514), strontium coloring it red, and barium green; so they are sometimes used in fireworks and signal flares. Two compounds of barium are of importance: barium chloride ($BaCl_2 \cdot 2\,H_2O$) and barium sulfate ($BaSO_4$). The former is used in the laboratory as a reagent for the detection of sulfate ions (p. 367); the latter is an insoluble white solid found in nature as the mineral *barite*, or *heavy spar*, and used in the manufacture of white paints, as well as in the drilling of oil and gas wells.

Barium sulfate in medicine. Barium sulfate has an interesting use in medicine. It is a very heavy material, and X-rays cannot penetrate it easily. When the physician wants a picture of the digestive tract (the stomach and intestines), the patient is asked to drink a suspension of barium sulfate in water. An X-ray photograph will then outline the entire tract, just as it outlines a bone.

RADIUM

For about a third of a century the element radium has been of the greatest interest to scientists and to everyone who has read the newspaper accounts of its wonderful properties and fabulous cost. The element belongs in this periodic family as its member of highest atomic weight.

But little is known of the chemical conduct of radium, and this little shows that in a chemical way radium is very like barium. It is the *physical* study of radium that fascinates us, so that an extended description of the element belongs to a text on physics rather than to one on chemistry.

A chapter devoted to radium will be found near the end of this text (Chap. LIII). It may be studied there or at this point, according to the wishes of teacher and pupil.

CHAPTER SUMMARY IN QUESTION FORM

1. State four ways in which calcium resembles sodium.

2. What are the properties of calcium that limit its use as a metal?

3. (*a*) What is the most abundant compound of calcium found in nature? (*b*) Write the names of six natural products (minerals or products of animals) that are composed entirely or largely of this compound. (*c*) Which of these six is the purest form of the compound?

4. Suppose you wish to prepare some pure calcium carbonate. (*a*) What compounds would you use in its preparation? (*b*) Write the equation for the reaction that takes place in its preparation. (*c*) State why the reaction goes to completion.

5. Write the formula (*a*) of the normal calcium carbonate; (*b*) of the acid calcium carbonate.

6. Contrast (*a*) the stability, and (*b*) the solubility in water, of the two carbonates referred to in question 5.

7. On page 513 you will find the statement that all normal carbonates except those of ammonium, sodium, and potassium are insoluble in water. (*a*) How do you explain the fact that the normal calcium carbonate *does* dissolve in ordinary soil waters?

8. Write the equation for the reaction that takes place (*a*) in the formation of caves; (*b*) in the formation of stalactites and stalagmites.

9. Discuss calcium oxide under the following heads: (*a*) formula; (*b*) common names; (*c*) process of making; (*d*) uses.

10. Discuss calcium hydroxide under the same heads as those of question 9.

11. (*a*) What is the distinction between gypsum and plaster of Paris? (*b*) For what is each used?

12. (*a*) How is calcium carbide prepared? (*b*) Write the equation for its reaction with nitrogen.

13. Prepare a table which gives the following information in regard to five important compounds of calcium:

CHEMICAL NAME	COMMON NAME, IF ANY	FORMULA	ONE USE	PREPARATION OR SOURCE

14. Give the name and formula for (*a*) a calcium compound used to lay dust on roads; (*b*) one used as a fertilizer; (*c*) one present in our bodies.

15. (*a*) Explain what is meant by the phrase *fixation of nitrogen.* (*b*) Give two important methods by means of which nitrogen is "fixed."

16. Barium sulfate is insoluble. What use is made of this property (*a*) in the laboratory? (*b*) in industry?

17. Oxidizable substances and nitrates are used in the manufacture of the red and green lights in fireworks. (*a*) What nitrates are used for this purpose? (*b*) Why not use sodium nitrate?

THOUGHT QUESTIONS

1. Some samples of Iceland spar and gypsum look very much alike. How could you distinguish between them?

2. Beads made of celluloid (p. 465) are often dyed and sold as coral beads. Suggest a way of detecting the fraud.

3. (*a*) What is the difference in composition between water-slaked lime and air-slaked lime? (*b*) Since the two products look alike, how could you distinguish between them?

4. Is the following reaction reversible, and, if so, how can you make it go in either direction?

$$CaCO_3 \longrightarrow CaO + CO_2$$

5. If you blow your breath through limewater, a white precipitate forms, but this precipitate disappears if you continue to blow through the liquid. If the resulting clear liquid is boiled, the white precipitate again forms. Account for (*a*) the formation of the precipitate, (*b*) its disappearance, and (*c*) its reappearance on boiling, writing the equations for the reactions involved.

6. Calculate the weight of water that would be required to slake 1 kg of lime.

7. A plant for the production of lime has an output of 30 tons of lime a day. Assuming the limestone to be pure calcium carbonate, what weight of limestone would the plant require daily?

OPTIONAL EXERCISES

1. Suppose you owned large quarries of limestone and wished to utilize this mineral in the manufacture of the products listed below. Write the equations for the reactions that would be involved in the preparation of each of these products from the limestone, assuming that the limestone is pure calcium carbonate: (*a*) lime; (*b*) hydrated lime; (*c*) mortar; (*d*) bleaching powder; (*e*) calcium carbide; (*f*) cyanamide.

2. Collect and exhibit to the class as many minerals (or other products) as possible that contain calcium.

CHAPTER XLV

The Magnesium Family

[A Group of New and Old Metals]

TABLE OF THE FAMILY

NAME OF ELEMENT	ATOMIC NUMBER	DENSITY	MELTING POINT	ELECTRONS IN ORBITS
Beryllium	4	1.8	1285°	2, 2
Magnesium . . .	12	1.74	651°	2, 8, 2
Zinc	30	7.14	419.4°	2, 8, 18, 2
Cadmium	48	8.6	320.9°	2, 8, 18, 18, 2
Mercury	80	13.546	– 38.87°	2, 8, 18, 32, 18, 2

An interesting family. Specimens of mercury have been found in Egyptian tombs dating back to at least 1500 B.C., but the metal was not used in Europe until about the beginning of the Christian Era. Zinc ores were smelted with copper ores to make brass centuries ago; but zinc was not recognized in Europe as a metal distinct from lead or tin until the middle of the eighteenth century. These two metals have a long history of usefulness.

Beryllium, magnesium, and cadmium were all obtained as solid metal particles about a century ago, but none of them has been of much importance as a metal until recent years. Even now their usefulness is largely in the future, although magnesium has many uses at the present time.

Each of the five metals has two valence electrons, as shown in the table, and hence acts as a bivalent metal in nearly all compounds. Mercury has some univalent compounds, and for several reasons it will be convenient to study this metal along with copper and silver.

MAGNESIUM

Let us start with magnesium. Magnesium is by far the most common and widely distributed of these elements. In nature it is found chiefly as silicate and carbonate minerals, in chloride and sulfate salt beds, and as ions in sea water.

Like sodium and calcium, magnesium is got by the electrolysis of its melted anhydrous chloride or of such compounds as the natural mineral carnallite (p. 524). It can be obtained also by heating magnesium oxide or carbonate with carbon in an electric furnace. It is the third most abundant of engineering metals, though it became important only after the World War.

Magnesium as a metal. The pure metal is silver-white. It is about two-thirds as heavy as aluminum, its density being 1.74. Because of surface oxidation it tarnishes to a gray color in air, and common acids dissolve it easily. It burns with a brilliant white flame in air, and so a mixture of powdered magnesium and an oxidizing agent is used in fireworks and signal flares (Fig. 400).

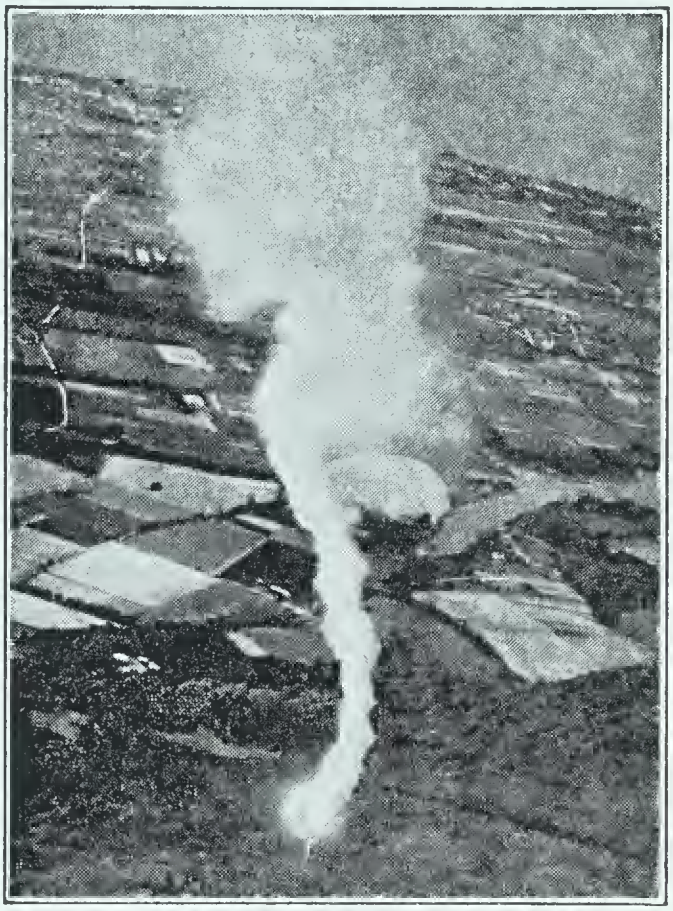
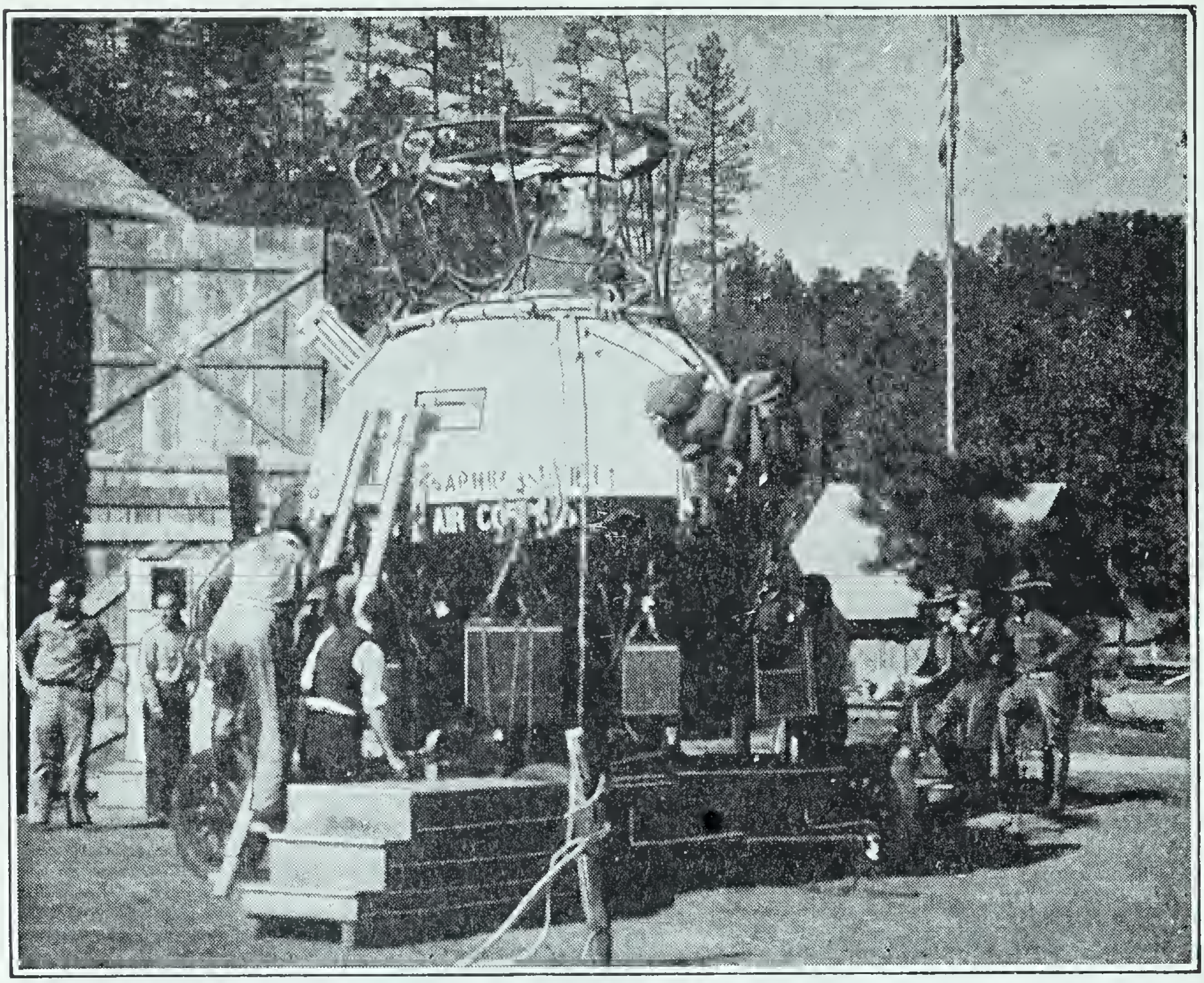


Fig. 400. Illumination by a magnesium flare dropped from an airplane

Photograph by United States Army Air Corps

Alloys of magnesium. The alloys of magnesium have been developed during the past twenty years. The best-known varieties are called *Dowmetals*, the Dow Chemical Company having developed the production and uses of magnesium and its alloys in this country. They contain from 85 per cent to 99 per cent of magnesium and are light, strong, easily machined, and weather-resisting. They can be cast, forged, rolled into plates, drawn into rods, or pressed into tubes. They are especially useful in replacing iron or copper where lightness is important, as in the body structure of automobiles and aircraft (Fig. 401), in home appliances, and even in many parts of machines, such as the pistons in gas engines.

Magnesium carbonate ($MgCO_3$). The carbonate is found in nature as the mineral *magnesite*. More often it is combined with calcium carbonate to form *dolomite* ($CaCO_3 \cdot MgCO_3$).



United States Army Air Corps

Fig. 401. The gondola in which Captain Stevens and Captain Anderson, on November 11, 1935, ascended 13¾ miles above the earth's surface

The gondola was made of Dowmetal, and its lightness made it possible for them to ascend 1500 feet higher than they could otherwise have risen

This mineral makes up whole mountain ranges and thick strata in the earth's crust.

Like calcium carbonate, magnesium carbonate dissolves in water containing carbonic acid and forms the acid salt $Mg(HCO_3)_2$. When heated, the carbonate decomposes into carbon dioxide and magnesium oxide, MgO. This is very like lime, and combines with water, or slakes, to form the hydroxide $Mg(OH)_2$. This solid, suspended in water, is called *milk of magnesia* and is used in medicine as a mild alkali. The oxide melts only at a very high temperature and for this reason is used as a lining for furnaces.

Magnesium silicates. A number of important silicates are found in nature. Among these are *talc*, or *soapstone*, and *asbestos*. Asbestos is mined in large quantities in the province of Quebec, Canada (Fig. 402), and is used in making a great variety of fireproof articles, such as boards, shingles, and

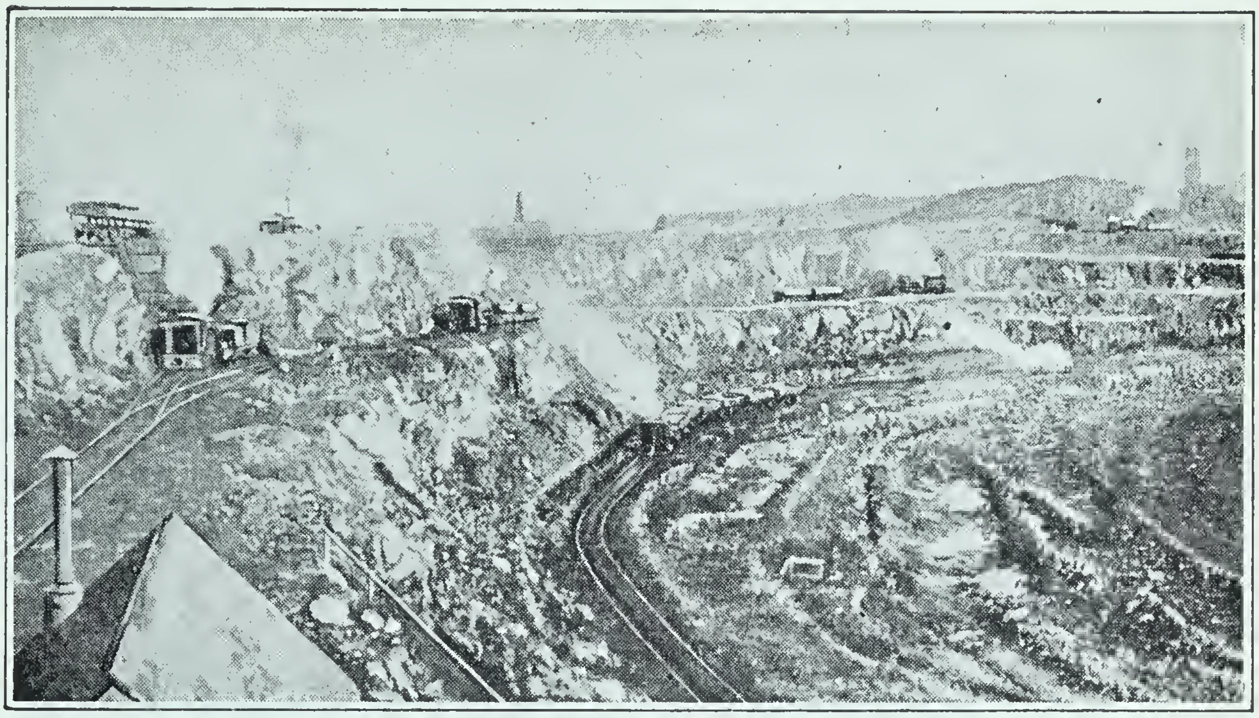


FIG. 402. Mining asbestos in Quebec, Canada

cloth; as a covering for hot-water and steam pipes to prevent loss of heat; and as an electrical insulator. Talc (soapstone) is used for making sinks and table tops in chemical laboratories. When ground to a powder, it is used for toilet purposes.

Some other compounds of magnesium. *Magnesium sulfate* (Epsom salts) ($MgSO_4 \cdot 7\ H_2O$); used in medicine, and for many other purposes, especially in the dye industry. *Magnesium chloride* ($MgCl_2 \cdot 6\ H_2O$); found in sea water and in salt beds. The anhydrous salt is used in getting metallic magnesium (p. 540). *Carnallite* ($KCl \cdot MgCl_2 \cdot 6\ H_2O$) (p. 524).

ZINC

Where zinc is found. Zinc is not found free in nature, nor do common rocks contain compounds of zinc. It is found in rich ores in very definite places (Fig. 403) and in a variety of minerals. Among these are *sphalerite* (ZnS), *smithsonite* ($ZnCO_3$), and *franklinite* ($ZnO \cdot Fe_2O_3$). The sulfide is often combined with other sulfides, and there are silicate ores as well. In the United States zinc is produced chiefly in Oklahoma, Kansas, Missouri, Montana, and New Jersey.

How zinc is got from its ores (metallurgy). The metallurgy of zinc is complicated. In a general way, the ores are roasted to get the metal into the form of oxide, and the oxide is then reduced with carbon and natural gas.

What zinc is like. With zinc we meet a metal that we all know something about. It is a bluish-white metal, about as heavy as iron. It melts at 419.4°, and vapors from the melted metal burn easily in air to form the oxide, ZnO. If it is worked between 100° and 150°, its crystalline habit is overcome, and it can be rolled into thin sheets. It then stays soft and malleable at ordinary temperatures. The granulated, or mossy, zinc of the laboratory is made by pouring melted zinc into water. In air the bright metal tarnishes to a gray color, but it does not oxidize further. It dissolves in all the common acids.

Uses of zinc. The chief use of zinc is in making *galvanized iron* (Figs. 405, 406). Sheet iron and iron pipes are preserved from rusting by a thin layer of zinc on their surfaces. Sometimes the covering film is deposited by blowing zinc vapor against the iron object. About two thirds of all the zinc produced is used in these ways.

Sheet zinc is used as a lining for sinks and water-containers, and as the cathode in dry cells. Large quantities of zinc are used in making various alloys, especially brass (Zn, Cu) and zinc bronze (Zn, Sn, Cu). In the laboratory we use zinc in making hydrogen and, in the form of a fine dust, as a reducing agent.

Zinc oxide (ZnO). The common way of making zinc oxide is to burn the vapor of zinc in air and filter out the white smoke of oxide in cloth bags. Commercially it is called *zinc white* and is used as a white pigment in paints. Many thousands of tons are used each year for this purpose. Unlike white lead, it is not changed in color by the sulfur compounds that are likely to be present in the air of a manufacturing town. These turn lead compounds black, owing to the formation of black lead sulfide. Zinc oxide is also used as a filler in rubber goods, especially in automobile tires.

Zinc sulfide (ZnS). As the mineral sphalerite, zinc sulfide is one of the most valuable ores of zinc. It is insoluble in water, and when made by precipitation it is pure-white in color. It is the only *white* insoluble sulfide. The very valu-

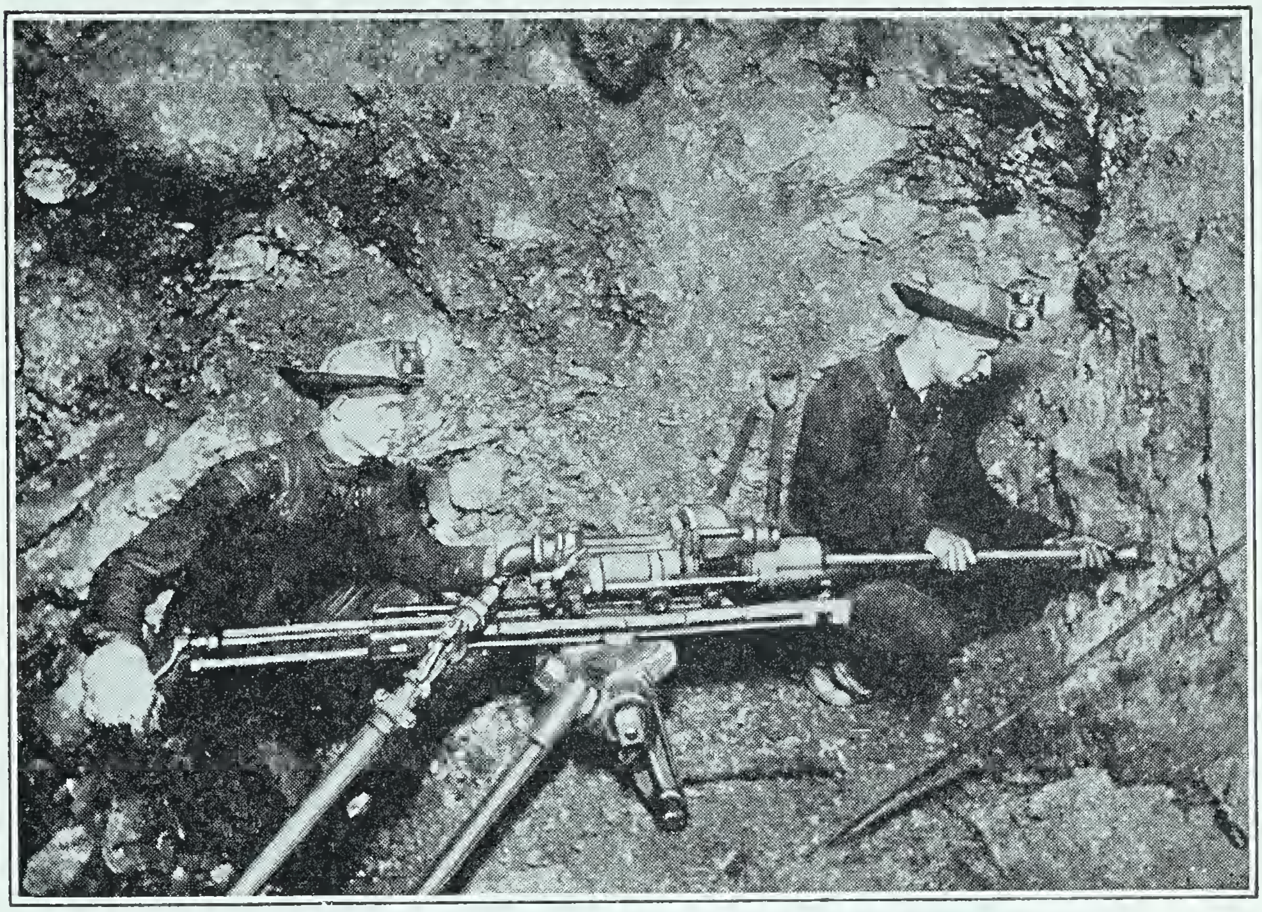


Fig. 403. Mining zinc and lead in Oklahoma

Fig. 404. Spraying a house with white paint containing zinc oxide and lithopone

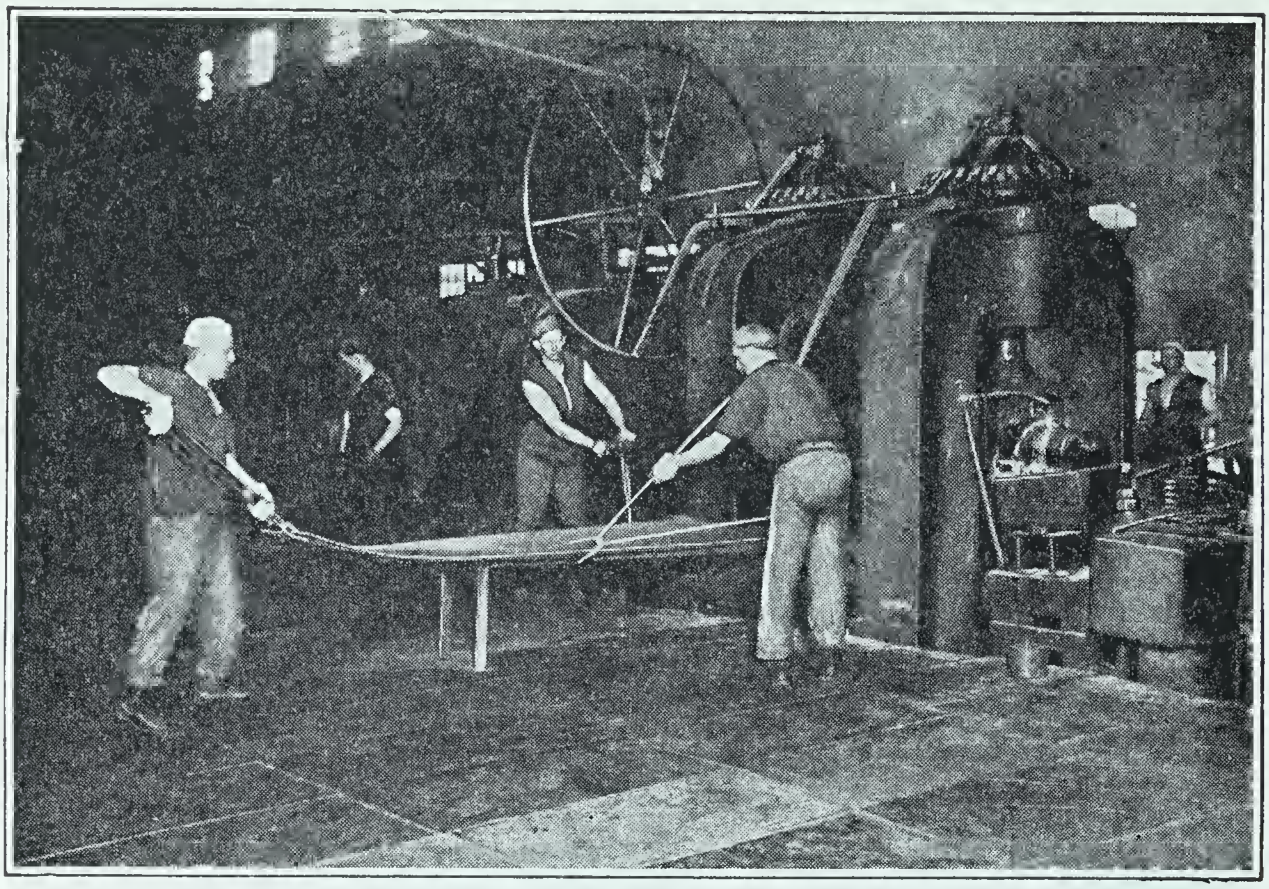


Fig. 405. Rolling sheet iron in preparation for galvanizing it with zinc

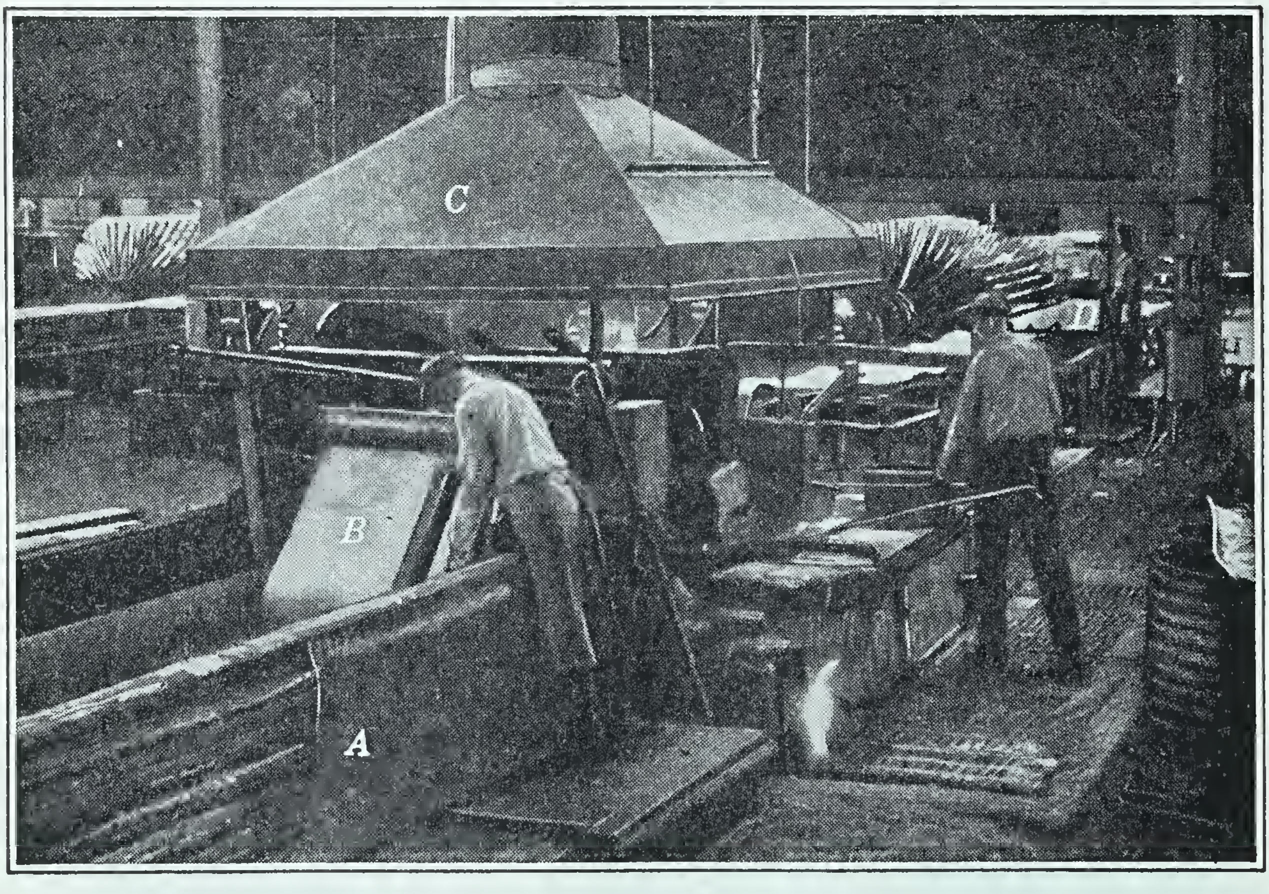


Fig. 406. Galvanizing sheet iron

The sheets of iron *B* are first cleaned by passing them through a vat *A* of dilute acid. They are then passed through a kettle of molten zinc, placed under the hood *C*, which carries away the poisonous fumes. The sheets are then passed between rollers, thus forming the finished product *D* able white paint pigment called *lithopone* is a mixture of zinc sulfide and barium sulfate (Fig. 404). It is made by bringing together solutions of barium sulfide and zinc sulfate:

$$BaS + ZnSO_4 \longrightarrow BaSO_4\downarrow + ZnS\downarrow$$

Other zinc salts. Zinc sulfate ($ZnSO_4 \cdot 7\ H_2O$), or *white vitriol*, is made by oxidizing zinc sulfide. It is used in making lithopone and in the dye industry. Zinc chloride ($ZnCl_2 \cdot 3\ H_2O$) is a deliquescent salt. It is used to preserve wood that must be partly buried, such as posts and railroad ties.

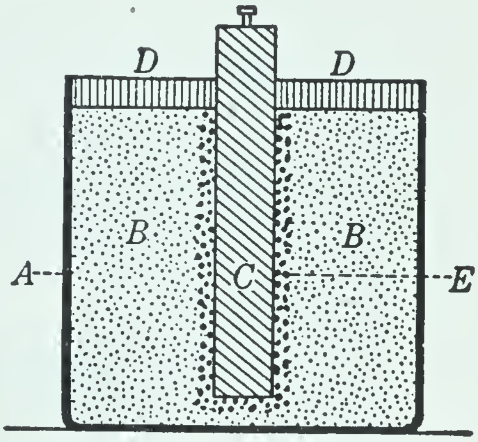


FIG. 407. Vertical section of a dry cell

Ion test for zinc. When added to a neutral solution of a zinc salt, a soluble sulfide precipitates *white* zinc sulfide, ZnS:

$$ZnCl_2 + Na_2S \longrightarrow 2\ NaCl + ZnS\downarrow$$

The dry cell. A dry cell is a little electric battery that will give a small current for short periods of time. Millions of these cells are used every year to operate door bells, call bells, telephones, and flashlights. They are made in the following manner:

A small can of thin sheet zinc *A* (Fig. 407) is filled with moist ammonium chloride *B*. In this is placed a carbon rod *C*, surrounded by a layer of manganese dioxide *E*. When the zinc container *A* (the anode) is connected to the carbon rod *C* (the cathode) by a wire, zinc dissolves as Zn^{++} ions. The electrons so set free from zinc atoms flow through the wire to the carbon rod. *This movement of the electrons through the wire constitutes an electric current.* Ammonium ions, NH_4^+, move through the electrolyte to the carbon rod, recover their missing electrons, and are at the same time oxidized by the manganese dioxide to form ammonia and water. The chloride ions, Cl^-, move toward the zinc electrode where they balance the charges of the Zn^{++} ions. The equation may be written thus:

$$Zn + 2\ NH_4Cl + MnO_2 \longrightarrow ZnCl_2 + 2\ NH_3 + Mn_2O_3 + H_2O$$

The ammonia formed in the reaction combines with the zinc chloride to make a solid compound which remains in the cell.

If manganese dioxide were not placed about the carbon rod, hydrogen would be set free and would be adsorbed on the rod. This results in a condition of the rod's surface called *polarization* which prevents the free release of the electrons to the approaching positive ions — diminishes the current passing.

CADMIUM AND BERYLLIUM

Cadmium. Cadmium is often present in ores of zinc and is got as a by-product in distilling zinc. It is very much like zinc, but is a heavier metal with a lower melting point (321°), and tarnishes less in the air. It has come into wide use for plating on other metals, particularly on small automobile parts. It is also used in a number of low-melting alloys and bearing metals.

Beryllium. The only important source of beryllium is the mineral *beryl*, which, unfortunately, contains only 4–5 per cent of the metal. In addition, it has proved very difficult to get the metal from this ore, and as yet no large production has been reached.

The future of the high-melting metal is likely to be that of an alloy metal, and most of the beryllium so far obtained has been alloyed with copper or, to a less extent, with aluminum. Beryllium-copper wears much better than pure copper, is harder, and can be made into springs. It is most valuable in electrical machines.

CHAPTER SUMMARY IN QUESTION FORM

1. When writing the formulas of the compounds of magnesium, zinc, and cadmium, of what advantage is it to know that these three elements belong to the same family?

2. Name the chief uses of magnesium.

3. Give the name of the mineral composed (*a*) of pure magnesium carbonate; (*b*) of magnesium carbonate combined with calcium carbonate.

4. Write the names and formulas of four important compounds of magnesium.

5. Write the equations for the action (*a*) of heat on calcium carbonate and magnesium carbonate; (*b*) of water on calcium oxide and magnesium oxide; (*c*) of hydrochloric acid on calcium carbonate and magnesium carbonate. (*d*) Point out the similarity between the compounds of calcium and magnesium as shown in the above equations.

6. What property has zinc that makes it useful (*a*) in the preparation of hydrogen? (*b*) in the manufacture of galvanized iron?

7. Give in tabular form the following information with respect to two of the most largely used compounds of zinc: (*a*) chemical name; (*b*) common name; (*c*) formula; (*d*) source; (*e*) industry using it.

8. Describe the chemistry of the dry cell.

9. What is the chief use (*a*) of cadmium? (*b*) of beryllium?

THOUGHT QUESTIONS

1. (*a*) Select from the electromotive series one univalent metal, one bivalent metal, and one trivalent metal that will replace hydrogen from acids. (*b*) Write the equation for the reaction of each of these metals with hydrochloric acid.

2. Write an equation showing how magnesium chloride, by hydrolysis can form magnesium hydroxide.

3. Magnesium carbonate and sodium bicarbonate are common medicines. One of the ingredients of the gastric juice in the stomach is hydrochloric acid. What reaction, if any, would take place in the stomach between these two compounds and hydrochloric acid?

4. The preceding chapter stated that large caves are often formed in limestone rocks. Discuss the possibility of having such caves formed in magnesite rocks.

5. Tell how you would proceed if you had a supply of zinc and wished to prepare the following compounds: (*a*) zinc oxide; (*b*) zinc chloride; (*c*) zinc sulfide.

6. Since magnesium compounds are so similar to calcium compounds, could you use magnesium hydroxide in place of calcium hydroxide in testing for carbon dioxide (p. 153)?

7. Why is it that a paint made from zinc oxide is not colored black by sulfur compounds?

8. What reaction, if any, should you expect if a strip of zinc were to be immersed in a solution of copper sulfate? Explain.

9. By what chemical test could you distinguish between soapstone and marble?

10. Lithopone is a mixture of barium sulfate and zinc sulfide. Is there any reason why a mixture of barium sulfide and zinc sulfate could not be used in place of lithopone?

11. Zinc oxide is often made by liberating zinc from its ores and then burning the zinc vapor in air. What weight of sphalerite would be required to make 6 tons of zinc oxide daily?

OPTIONAL EXERCISES

1. Obtain a dry cell (a worn-out flashlight battery will do); take it apart and examine its structure. Explain its parts and action to the class.

2. How many liters of hydrogen are liberated when 650 g of zinc is dissolved (*a*) in hydrochloric acid? (*b*) in sulfuric acid?

CHAPTER XLVI

Aluminum

[The Metal a Boy Gave to the Industrial World]

The story of aluminum. The story of aluminum might be called "A Boy's Dream Come True." A hundred years ago aluminum could be bought as a museum specimen for about ninety dollars a pound. About fifty years ago, by using metallic sodium in its preparation, nearly one hundred pounds was produced in one year, worth five dollars a pound. There was plenty of aluminum in the rocks, much more than there is of iron (p. 29), but it was very costly to free it from its compounds.

One day in 1886, in a classroom in Oberlin College, Professor Jewett told his class that whoever should solve the problem of cheap aluminum would be a benefactor to humanity and make a great fortune. Young Charles Hall (Fig. 15) determined he would be that man, and that very summer, just after graduation, he began to work on the problem.

Now the production of relatively cheap sodium had been solved by electrolysis of its melted salts (p. 233), and many chemists had tried to get aluminum in a similar way, but with no success. Nor had they any luck with melted cryolite, a low-melting mineral from Greenland having the formula Na_3AlF_6.

After many vain attempts young Hall began to reason in this way: The thing to do is to find some *melted salts* in which aluminum oxide will *dissolve* and in which it will *act as an electrolyte.* So he secured a sample of cryolite, melted it in a crucible in a homemade furnace in the woodshed, and sprinkled some aluminum oxide on the liquid. *It promptly dissolved.* Was it an electrolyte? He had a few old batteries ready and dipped their electrodes into the crucible. The current passed readily, and after a time the crucible was cooled and its contents examined. It contained *little beads of aluminum,* which Hall carried in triumph to show to Professor Jewett.

The rest of the story concerns patents, litigation, and financing a great business. In prewar years the annual production of new aluminum by the Hall process (Fig. 408) has been as high as one hundred and fifty thousand tons, with a sales price of about twenty cents a pound. It is pleasant to know that *both* of Professor Jewett's prophecies came true.

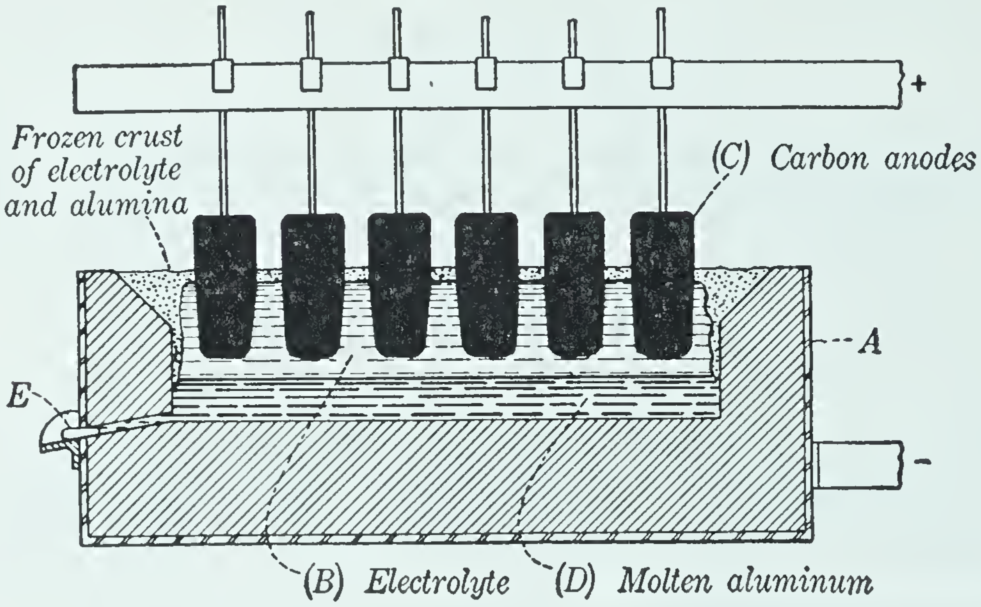


FIG. 408. The electrolytic production of aluminum (Hall process)

An iron box *A* is connected as cathode with a powerful electric generator, and a row of carbon anodes, *C*, dip into the box. Cryolite is melted in the box by its resistance to the current. Aluminum oxide, obtained from bauxite, is added from time to time and acts as an electrolyte, aluminum being liberated at the cathode and oxygen at the anodes. The temperature is kept above the melting point of aluminum, and the liquid metal collects under the lighter cryolite bath. The metal is drawn off at *E* from time to time

Aluminum is an abundant element. Only two elements, namely oxygen and silicon, are more abundant than aluminum. The earth's crust is more largely made up of feldspars than of any other mineral, and these are all silicates of aluminum together with sodium, potassium, or calcium. For the most part, soils have been formed by the weathering of such rocks; so they are rich in silicates of aluminum, chiefly as *clay* (p. 403). Two other important minerals are *cryolite* (Na_3AlF_6) and *bauxite*, a mixture of hydrated aluminum oxides ($Al_2O_3 \cdot H_2O$ and $Al_2O_3 \cdot 3\ H_2O$) mixed with similar compounds of iron. Bauxite is the ore from which aluminum is made, and in this country it is found chiefly in Arkansas (Fig. 409).

Aluminum the metal. We all know that aluminum has many good properties. It is a silver-white metal, only about

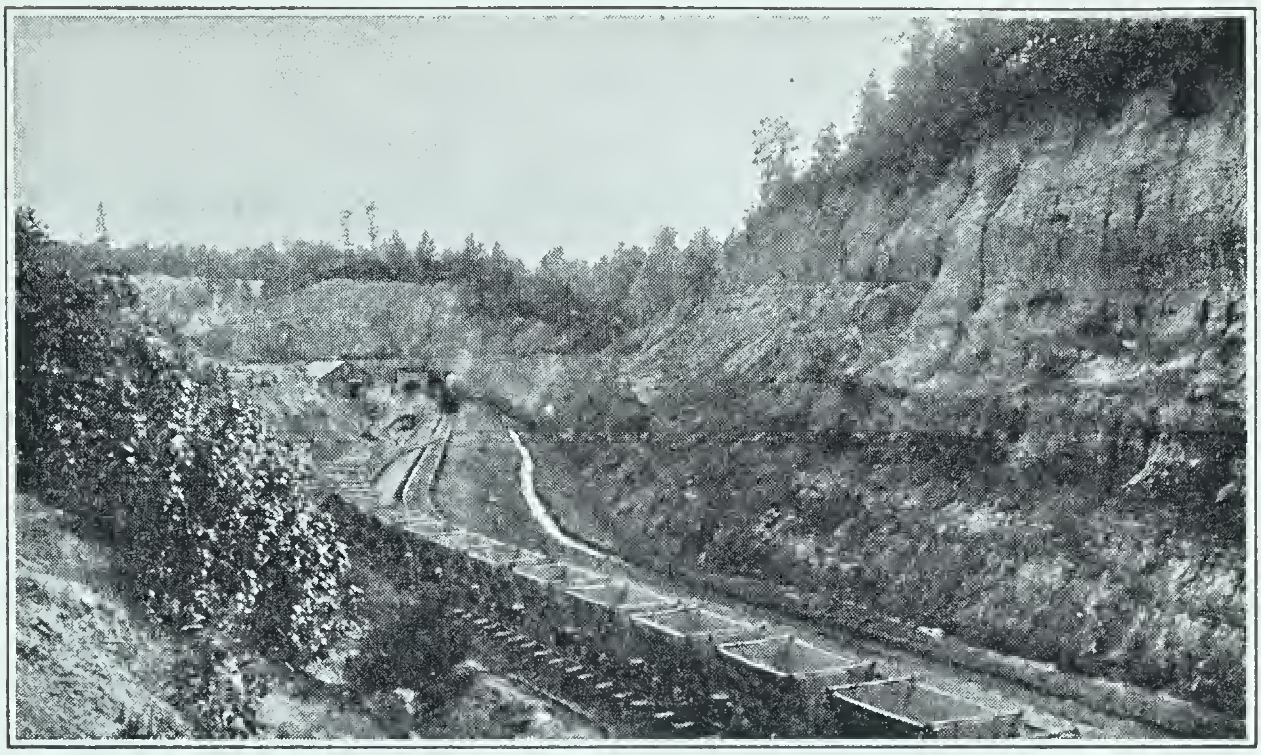


FIG. 409. Mining bauxite in Arkansas

one-third as heavy as iron. It can be rolled into plates or even into very thin foil, drawn into wire, cast in molds, forged, and welded. It is fairly hard and strong, and is a good conductor of heat and electricity.

Neither air nor boiling water acts upon it beyond forming a very thin invisible covering of oxide, which stops the action (like a coat of varnish). Many aluminum articles are now given a coating of this kind by electrolysis. At higher temperatures it burns in oxygen, setting free a great deal of heat; and so it is a very good reducing agent. It is easily attacked by most acids and by strong alkalies, and is corroded by salt water.

Uses of aluminum. Such a metal has many uses. Because of its lightness and fair strength it is replacing sheet iron in the body parts of carriers for all kinds of transportation, — air, land, and water, — and such uses take about 40 per cent of the output (Fig. 410).

Its lightness and electrical conductance fit it for trolley and power lines and for all sorts of electrical appliances, and this is its second-greatest use. To carry a given current, aluminum wires need be only half as heavy as copper wires; so the supports can be further apart. Its next-greatest use is for all sorts of kitchen utensils and small household appliances. It is ideal for such uses; for it is stiff, easily polished, does not rust, and is not poisonous. A good deal of aluminum is used in making steel, for hardware in the building trade, to make aluminum paint for covering such iron articles as steam radiators, and even to make ink for printing. The photoflash lamps (Fig. 18) now in general use for making flashlight pictures consist of a bulb (resembling an electric-light bulb) filled with aluminum foil and oxygen. The foil is ignited by a fuse heated by a pocket battery.

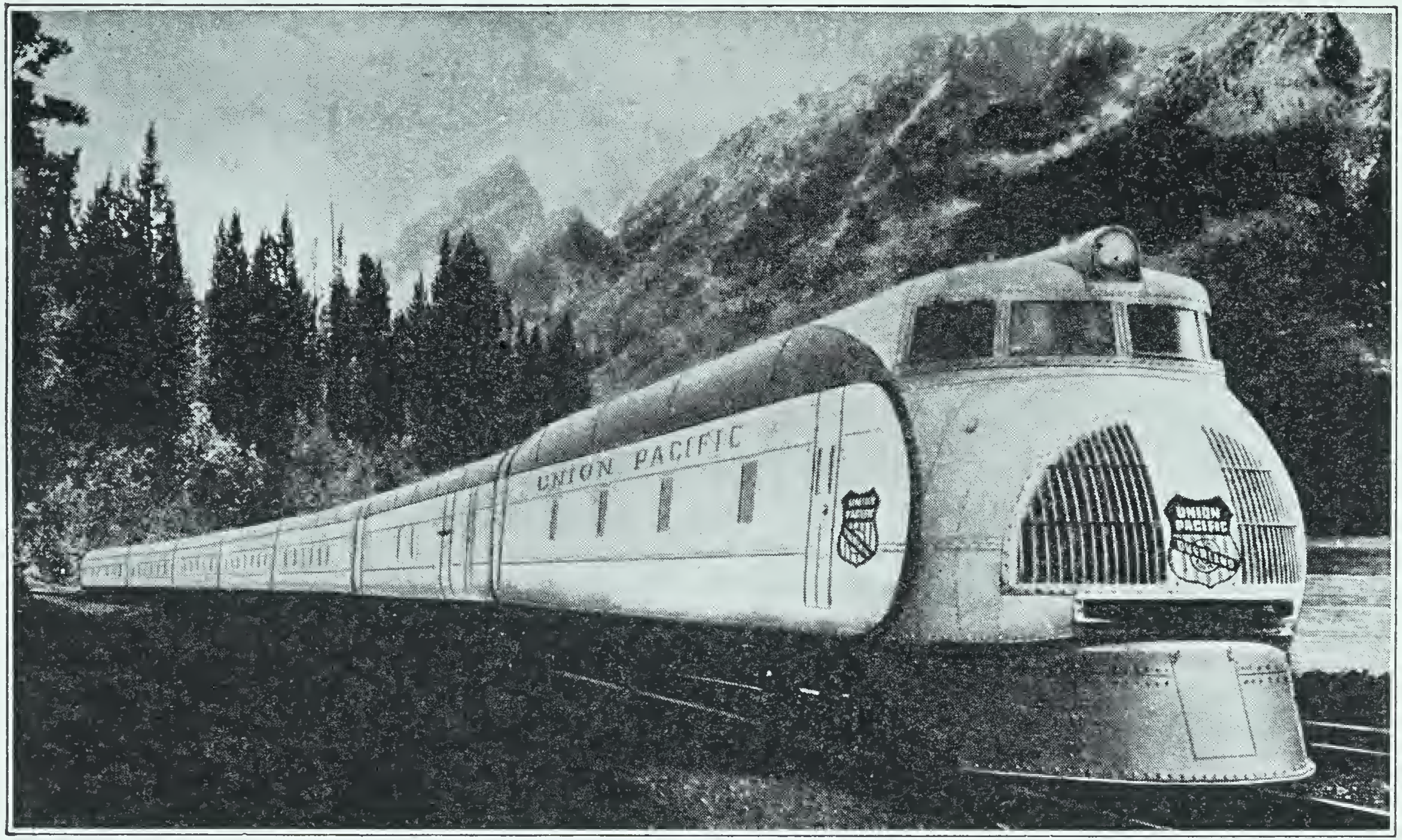
Aluminum alloys. Increasing amounts of aluminum are used as alloys rather than as simple metal. This is for the sake of getting more strength than the pure metal has. For example, the frames of airships and the wings and even the bodies of airplanes are often made of *duralumin*, an alloy of about 95 per cent aluminum with about 4 per cent copper and 0.5 per cent each of manganese and magnesium. It is about as strong as steel. *Magnalium* (aluminum with 8 to 12 per cent of magnesium) is very light in weight and silvery in appearance. *Aluminum bronzes* consist of copper alloyed with 8 to 10 per cent of aluminum, and we have seen that *Dowmetals* nearly all contain aluminum.

Goldschmidt reduction process. Some of the metals are hard to get in pure state by reduction of their oxides with carbon, because, like calcium, they form carbides instead of free metals (p. 534). The German chemist Goldschmidt invented the use of powdered aluminum as a reducing agent in such cases. For example, chromium or manganese can be made as shown in the equation

$$Cr_2O_3 + 2\ Al \longrightarrow Al_2O_3 + 2\ Cr$$

A great deal of heat is set free in these reactions, and the reduced metal collects as a small ingot under the melted aluminum oxide. The process is used for small quantities only, and electrical methods are better in most cases.

Welding by the use of aluminum. The great heat set free in the reduction of oxides by aluminum is turned to practical account in welding broken iron parts. The welding of street-car rails is another example. The ends of the rails are thoroughly cleaned and are brought nearly together in line.



Aluminum Company of America

FIG. 410. The streamline "all-aluminum" train *City of Los Angeles*, constructed almost entirely of alloys of aluminum and of iron

Equipped with Diesel engines and shaped so as to diminish the resistance of air, this train easily maintains a speed of over 100 miles per hour and makes the trip from Chicago to Los Angeles in $39\frac{3}{4}$ hours

A sand mold *A* (Fig. 411) is clamped about the joint. Just over the joint is placed the crucible *B*, which holds a mixture of iron oxide and powdered aluminum. The rail ends are next heated to redness with a gasoline torch (or by electrical resistance). Then the mixture in the crucible is set on fire, and the iron oxide is reduced to liquid iron:

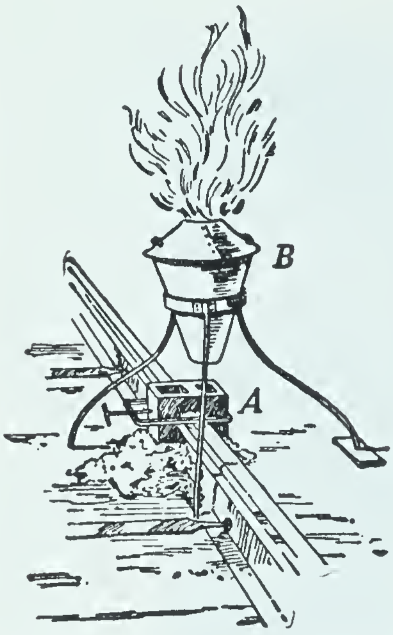


FIG. 411. Welding car rails with thermite

$$Fe_2O_3 + 2\ Al \longrightarrow Al_2O_3 + 2\ Fe$$

After a few seconds the crucible is opened at the bottom, and the liquid iron is run into the mold and the space between the ends of the rails, making a perfect weld.

One of the largest welds ever made was that of the sternpost of the army transport *Northern Pacific*, which was broken when the ship ran aground in a fog (Fig. 412). A mixture of aluminum powder and metallic oxides ready for use is sold under the name *thermite.*

Aluminum oxide, Al_2O_3. The atom of aluminum has the structure shown in Fig. 413. It has *three* valence electrons, and is trivalent in all its compounds. In nature the oxide is found in a number of crystalline forms, perhaps the hardest natural products except the diamond. In color they range from nearly colorless *corundum*, blue *sapphire*, red *ruby*, yellow *Oriental topaz*, and violet *Oriental amethyst* to brown or black *emery*. These different colors are due to

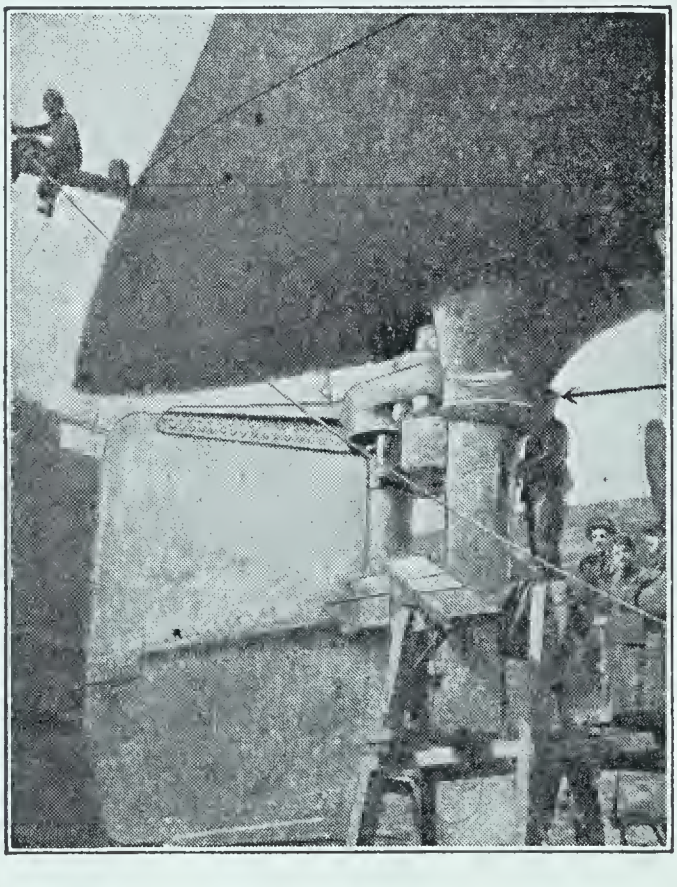


FIG. 412. The stern of the *Northern Pacific*

The picture shows the broken post after being welded by thermite (the break is at the point indicated by the arrow) traces of various metallic oxides dissolved in crystals of corundum. Emery in the form of grindstones or powder is used for grinding and polishing metals. An artificial oxide called *alundum* can be used instead of emery, and is also made into furnace linings and crucibles. The melting point of the oxide is very high.

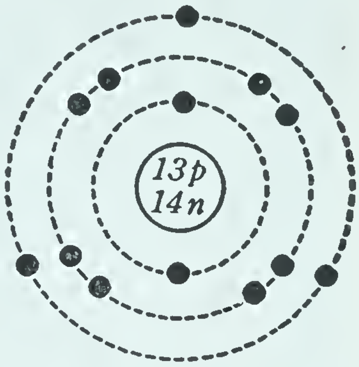


FIG. 413. The aluminum atom

Artificial gems. Chemists have succeeded in making crystals of corundum in small furnaces (Fig. 414), and coloring them with small percentages of metallic oxides in a great variety of colors. These are artificial gems. They are identical in color, hardness, and crystal properties with the costly natural gems named in the last paragraph.

Aluminum hydroxide ($Al(OH)_3$). When ammonium hydroxide is added to a solution of any aluminum salt, a white jellylike compound is precipitated which we may regard as the hydroxide $Al(OH)_3$:

$$AlCl_3 + 3\ NH_4OH \longrightarrow 3\ NH_4Cl + Al(OH)_3\downarrow$$

This precipitate varies somewhat in formula, because it is a colloidal gel (p. 418). As will be explained later, its gelatinous nature makes it useful in water purification and in the dye industry. It is a very weak base; so its salts are all acid to indicators.

Amphoteric hydroxides. When aluminum hydroxide is treated with an *acid*, we get the expected salt:

$$Al(OH)_3 + 3\ HCl \longrightarrow AlCl_3 + 3\ H_2O$$

When it is treated with a *strong alkali*, it dissolves, and in the solution we find a salt of the formula Na_3AlO_3:

$$Al(OH)_3 + 3\ NaOH \longrightarrow Na_3AlO_3 + 3\ H_2O$$

This salt is called *sodium aluminate*, and gives the ions $3\ Na^+$ and AlO_3^{---}. So *aluminum hydroxide can act either as a weak base or as a weak acid. Such a hydroxide is called an amphoteric hydroxide*, which means that it acts both ways.

An amphoteric hydroxide is one that can act either as an acid or as a base.

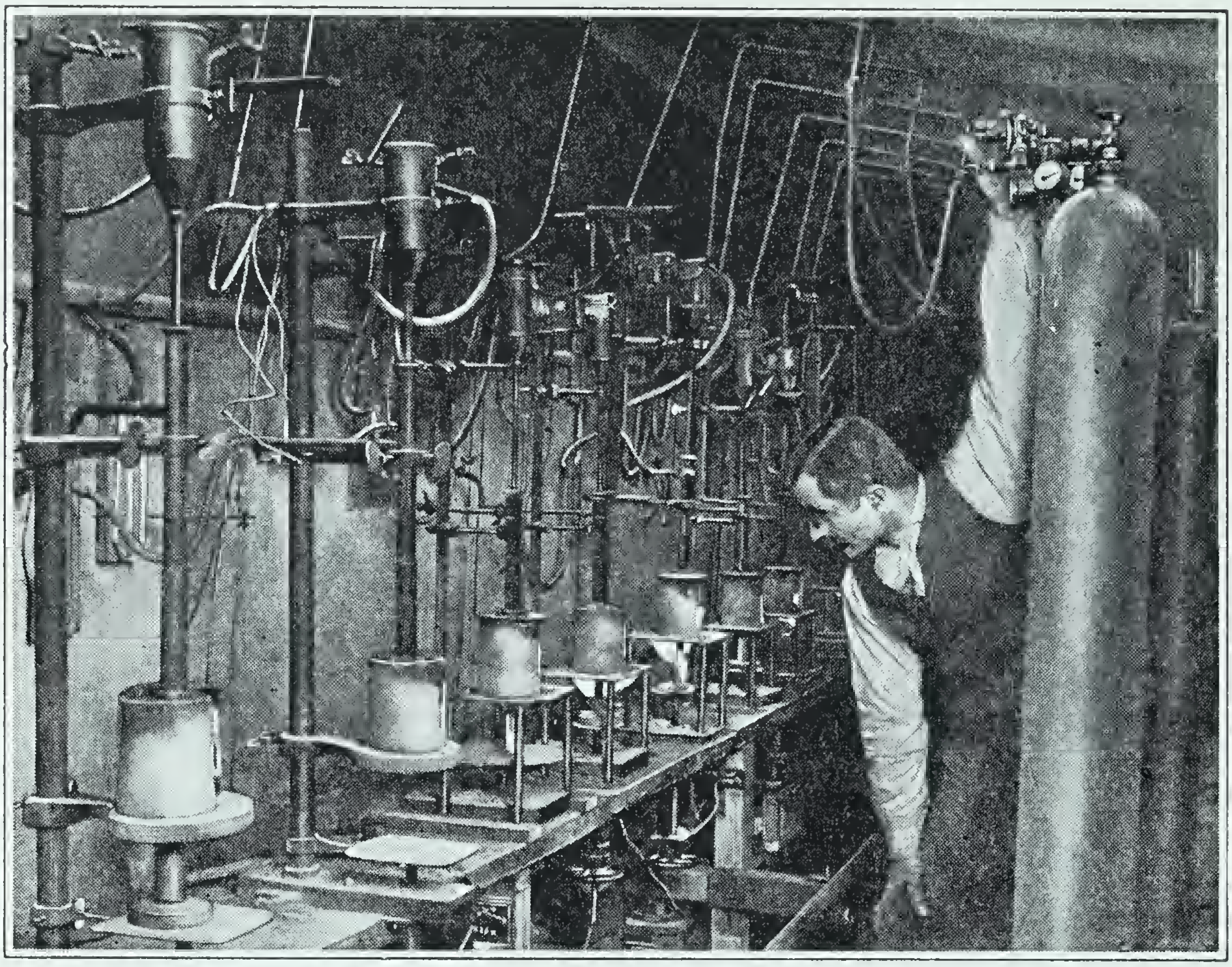


FIG. 414. A row of furnaces used in making artificial rubies

Oxygen is used to obtain high temperatures

Aluminum sulfate ($Al_2(SO_4)_3$). This compound is made by heating bauxite with sulfuric acid. Under ordinary conditions it crystallizes from water as the hydrate $Al_2(SO_4)_3 \cdot 18\ H_2O$. It is the cheapest salt of aluminum, and every year several hundred thousand tons of it are made in this country for use in water purification, dyeing, paper-making, and baking powders, and for making other aluminum compounds.

The alums. If aluminum sulfate is crystallized from solutions containing a sulfate of an alkali metal, it forms a *double salt* called an *alum*. With potassium sulfate the equation is

$$K_2SO_4 + Al_2(SO_4)_3 + 24\ H_2O \longrightarrow 2\ KAl(SO_4)_2 \cdot 12\ H_2O$$

The sulfates of some other trivalent metals form similar compounds with the alkali sulfates, and these are all called alums. They all crystallize in eight-sided crystals with 12 molecules of water of hydration. Examples:

Potassium alum	$KAl(SO_4)_2 \cdot 12\ H_2O$
Ammonium alum	$NH_4Al(SO_4)_2 \cdot 12\ H_2O$
Chrome alum	$KCr(SO_4)_2 \cdot 12\ H_2O$

Hydrolysis of salts of aluminum. Since aluminum hydroxide is a very weak base, its salts, even those with *strong* acids, are somewhat hydrolyzed. Its salts with *weak* acids go to pieces *completely* in water.

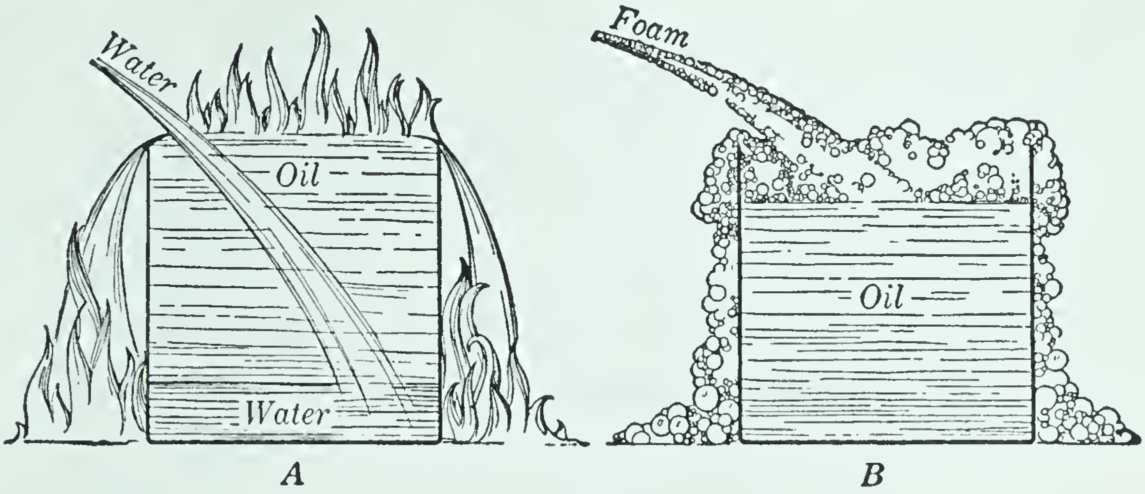


FIG. 415. The comparative use of water and "foam" in extinguishing oil fires

The water, *A*, does not mix with the oil, and being heavier than the oil sinks to the bottom, so that the oil continues to burn. The "foam," *B*, on the other hand, floats on the oil and smothers the flame by preventing the oxygen of the air from coming into contact with the oil

For example, when an aluminum salt and a soluble carbonate are brought together in solution, we should expect to have aluminum carbonate precipitating (since nearly all carbonates are insoluble (p. 513)):

$$Al_2(SO_4)_3 + 3\,Na_2CO_3 \longrightarrow Al_2(CO_3)_3\downarrow + 3\,Na_2SO_4$$

But if it is formed at all, it instantly hydrolyzes into aluminum hydroxide and carbonic acid:

$$Al_2(CO_3)_3 + 6\,H_2O \longrightarrow 2\,Al(OH)_3 + 3\,H_2CO_3$$
$$H_2CO_3 \longrightarrow H_2O + CO_2\uparrow$$

The fact that aluminum sulfate sets carbon dioxide free from a carbonate has been turned to use in inventing a kind of fire extinguisher, as well as in making some of the baking powders now in use.

"Foam" fire-extinguishers. A "foam" extinguisher is similar in design to that shown in Fig. 109. But it has a solution of aluminum sulfate in place of sulfuric acid, carbon dioxide being set free by the action of the aluminum compound on the sodium bicarbonate. The two solutions also contain some gummy substance that will hold the escaping carbon dioxide as a foam when they are mixed together. The foam is made up of bubbles of the gummy liquid filled with carbon dioxide. It is very effective in fighting oil fires (Fig. 415).

How dough is made "light" for baking. In making baked foods, such as bread, biscuits, and cakes, from dough, some substance must be in the dough that will slowly set free bubbles of carbon dioxide. This is to make the dough into a light, spongy mass before and during the baking. Carbon dioxide is provided in the following ways:

1. ***By alcoholic fermentation.*** As we have seen, this is the method generally used in making bread (p. 474).

2. ***By the action of sour milk on sodium bicarbonate.*** The lactic acid in the sour milk (p. 458) slowly acts on the bicarbonate, setting free carbon dioxide:

$$H \cdot C_3H_5O_3 + NaHCO_3 \longrightarrow NaC_3H_5O_3 + H_2O + CO_2\uparrow$$

3. ***By baking powders.*** Every baking powder is made up of three kinds of things: (1) sodium bicarbonate, to supply the necessary carbon dioxide; (2) some compound which, *along with water*, will slowly set carbon dioxide free from the bicarbonate; and (3) starch or flour to give body to the powder and absorb any moisture that may get to it from the air.

The compounds used to set free the carbon dioxide are (*a*) cream of tartar, sometimes mixed with tartaric acid (p. 479); (*b*) an acid phosphate, usually $Ca(H_2PO_4)_2 \cdot H_2O$; or (*c*) sodium aluminum sulfate, $Na_2SO_4 \cdot Al_2(SO_4)_3$.

The reactions of baking powders. The reactions that take place when water is added to each kind of baking powder are as follows:

Cream of tartar:

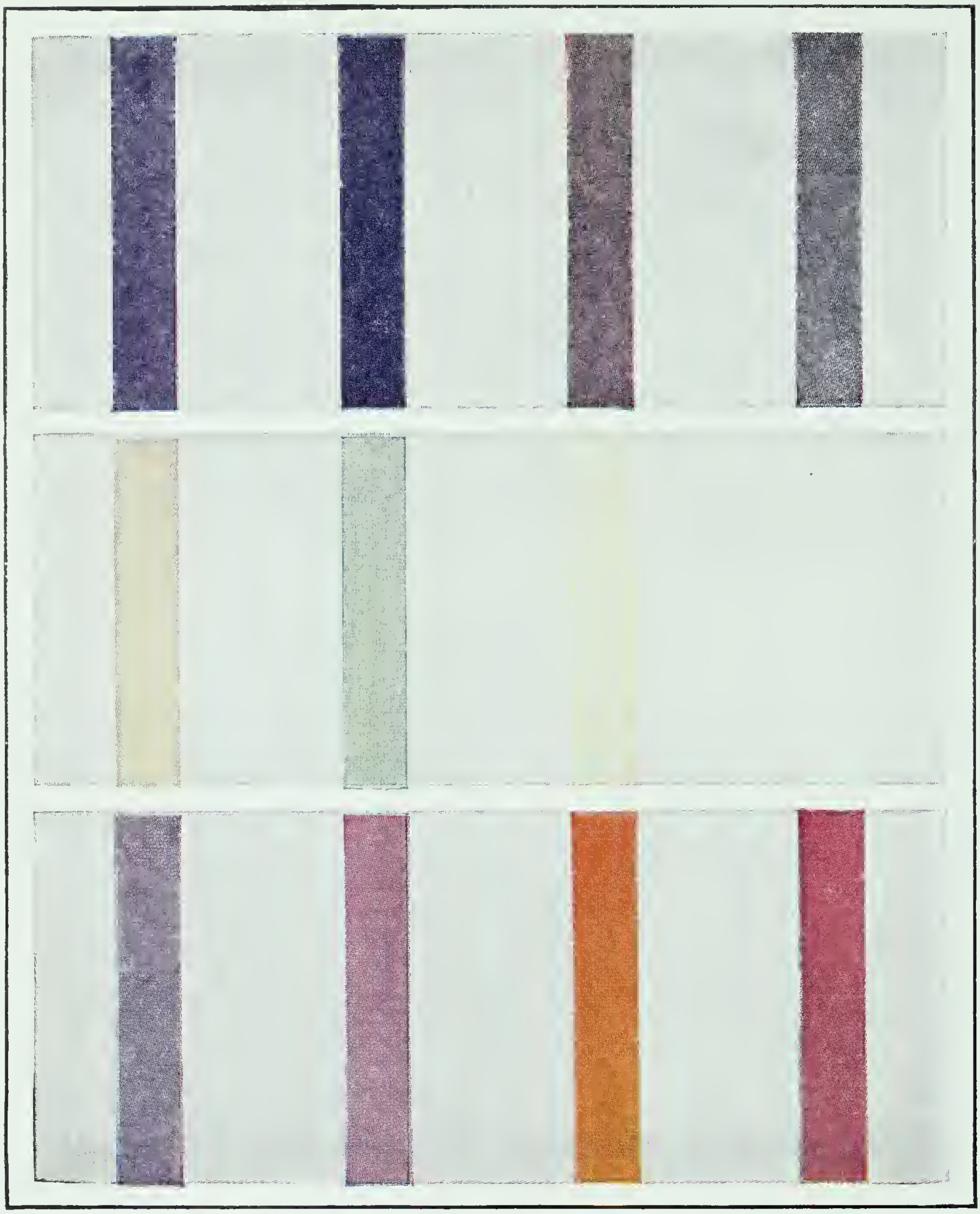
$$KHC_4H_4O_6 + NaHCO_3 \longrightarrow KNaC_4H_4O_6 + H_2O + CO_2\uparrow$$

Phosphate:

$$\begin{aligned}&Ca(H_2PO_4)_2 + 2\ NaHCO_3\\&\qquad\longrightarrow CaHPO_4 + Na_2HPO_4 + 2\ H_2O + 2\ CO_2\uparrow\end{aligned}$$

Sodium aluminum sulfate:

$$\begin{aligned}&Na_2SO_4 \cdot Al_2(SO_4)_3 + 6\ NaHCO_3\\&\qquad\longrightarrow 2\ Al(OH)_3 + 4\ Na_2SO_4 + 6\ CO_2\uparrow\end{aligned}$$



THE USE OF MORDANTS IN DYEING

The central panel in the figure represents a piece of white cotton cloth. Four mordants, one of iron, one of chromium, one of tin, and one of aluminum, have been applied to the cloth in four vertical stripes (leaving the spaces between without a mordant). The upper panel shows the same cloth after being dyed with gallein; the lower panel shows a similar piece of cloth after being dyed with alizarin

What is a dye? On page 487 we learned something about aniline dyes and the history of their discovery and development. Because of the great variety and purity of their colors, these manufactured dyes have almost wholly taken the place of those formerly got from plants and trees.

A good dye must have these qualities: (1) it must have a good color; (2) it must not injure the cloth; (3) it must *dye fast* — that is, after the cloth has been dyed it must keep its color when washed; (4) it must not fade too easily — must be reasonably *sun-fast.*

The process of dyeing. In successful dyeing the color must be fixed evenly and permanently on the cloth. As a rule the animal fibers, wool and silk, are more easily dyed than the vegetable fibers, such as cotton and linen. With most dyes it is only necessary to steep a cloth of wool or silk in a solution of the dye.

Cotton cloths treated in this way will become colored, but with most dyes the color is not fast and will wash out. In such cases the cloth is dyed with the use of a *mordant.*

Dyeing with a mordant. The cloth is first soaked in a solution of some salt which is easily hydrolyzed and which then forms an insoluble gelatinous hydroxide. For example, the cloth is first soaked in a solution of aluminum sulfate, and then hung up and steamed. This hydrolyzes the salt, forming colloidal aluminum hydroxide *inside the fibers of the cloth.* The cloth is then steeped in the dye, which is adsorbed by the aluminum hydroxide within the fibers. This "fixes" it upon the cloth.

Mordants. Aluminum hydroxide, and many other colloidal compounds that act in the same way, are called *mordants.* The same dye will often give different colors with different mordants (see color plate opposite this page). So skill is needed in choosing the mordant as well as the dye.

Lakes. The same compounds that are useful as mordants may be precipitated in solutions of various dyes, and the *precipitate* will then be dyed fast. Its color may not be the same as that of the dye. Colored precipitates of this kind are called *lakes,* and are used as paint pigments.

CHAPTER SUMMARY IN QUESTION FORM

1. Aluminum, at one time selling at $90 or more per pound, is now worth about 20 cents per pound. Name the man, the process, and the compound largely responsible for this reduction in price.

2. (*a*) Name four forms in which aluminum occurs in nature. (*b*) Which of these are used in the commercial production of aluminum?

3. Why is aluminum prepared from the rather rare mineral bauxite, instead of from clay, which is everywhere abundant?

4. Name five properties of aluminum that make it very valuable for many uses.

5. (*a*) Name the alloy that is so largely used in the construction of airships and airplanes. (*b*) What metals are present in this alloy?

6. What property have aluminum and carbon in common that makes them useful in separating metals from their ores?

7. Aluminum is much more expensive than carbon. Why, then, is it sometimes used rather than carbon in separating metals from their ores?

8. (*a*) What is thermite, and (*b*) for what is it used?

9. (*a*) State the valence of aluminum, and (*b*) write the formulas for the normal aluminum salt of each of the following acids: hydrochloric; sulfuric; phosphoric.

10. What is an amphoteric hydroxide?

11. Aluminum hydroxide is a very weak base. Why should you expect the salts of aluminum to hydrolyze readily?

12. (*a*) What compound is formed when ammonium hydroxide is added to a solution of any aluminum salt? (*b*) The gelatinous character of the compound formed makes the compound useful for what purposes?

13. Give the name and formula for the cheapest of the soluble compounds of aluminum.

14. (*a*) Give the name and formula of the common alum. (*b*) Do all alums contain aluminum?

15. When a solution of sodium carbonate is added to a solution of an aluminum salt such as aluminum sulfate, carbon dioxide is evolved. Account for the formation of this gas by writing the equations for the reactions that take place between sodium carbonate and aluminum sulfate.

16. What use is made of the fact that carbon dioxide is evolved in the reaction referred to in question 15?

17. (*a*) Name three methods for making dough light. (*b*) What is the aerating agent in each of these methods?

18. (*a*) Name two compounds present in all baking powders. (*b*) Name three other compounds at least one of which must also be present.

19. Name the four requisites of a good dye.

20. Tell what is meant by the words (*a*) *lake*, (*b*) *mordant.*

THOUGHT QUESTIONS

1. Name two important chemical discoveries made by young men.

2. Why do the directions for using aluminum cooking vessels state that such utensils should not be washed with strong soaps?

3. When baking soda is heated, carbon dioxide is evolved (p. 521). Why not, then, use it alone as an aerating agent?

4. Does the question as to whether a baking powder is injurious to health depend only on the compounds that constitute the powder?

5. What compounds remain in biscuits as a result of the use of each of the different kinds of baking powders?

6. (*a*) Would a mixture of sweet milk and soda serve just as well as a mixture of sour milk and soda for purposes of aerating? (*b*) Give the reason for your answer.

7. What is the difference between baking powder and baking soda?

8. Can you suggest any reason why baking powder is not used in baking loaves of bread?

9. Do you think that a mixture of baking soda and the juice of grapefruit would act as an aerating agent?

10. Which should you expect to hydrolyze the more readily, aluminum sulfate or aluminum carbonate? Why?

11. Should you expect a water solution of aluminum sulfate to be acid, neutral, or basic?

12. An aluminum plant has a daily output of 20,000 kg of the metal daily. What weight of aluminum oxide would be required daily?

13. What weight of water of hydration is present in 1 kg of potassium alum?

OPTIONAL EXERCISES

1. Ordinary cream-of-tartar baking powders contain about 12 per cent of starch or flour, the other 88 per cent consisting of baking soda and cream of tartar mixed in the proper proportions. Refer to the equation for the reaction of cream-of-tartar baking powders (p. 558), and calculate the number of grams of (*a*) starch, (*b*) baking soda, and (*c*) cream of tartar required to make 500 g of baking powder. Obtain the required weights of the pure substances and make, say, 500 g of the powder for use in your home. (The ingredients must be thoroughly mixed.)

2. (*a*) What is the ratio between the number of gram-molecular weights of baking soda used in a baking powder and the number of gram-molecular weights of carbon dioxide liberated (see equations, p. 558)? (*b*) Calculate the volume of carbon dioxide liberated from 1 gram-molecular weight of baking soda if the temperature of the gas is 150°. (For method of changing volume at 0° to volume at 150°, see page 43.)

CHAPTER XLVII

Pure, Soft Water on a Large Scale

[A Problem of Health, Home Comfort, and Industrial Need]

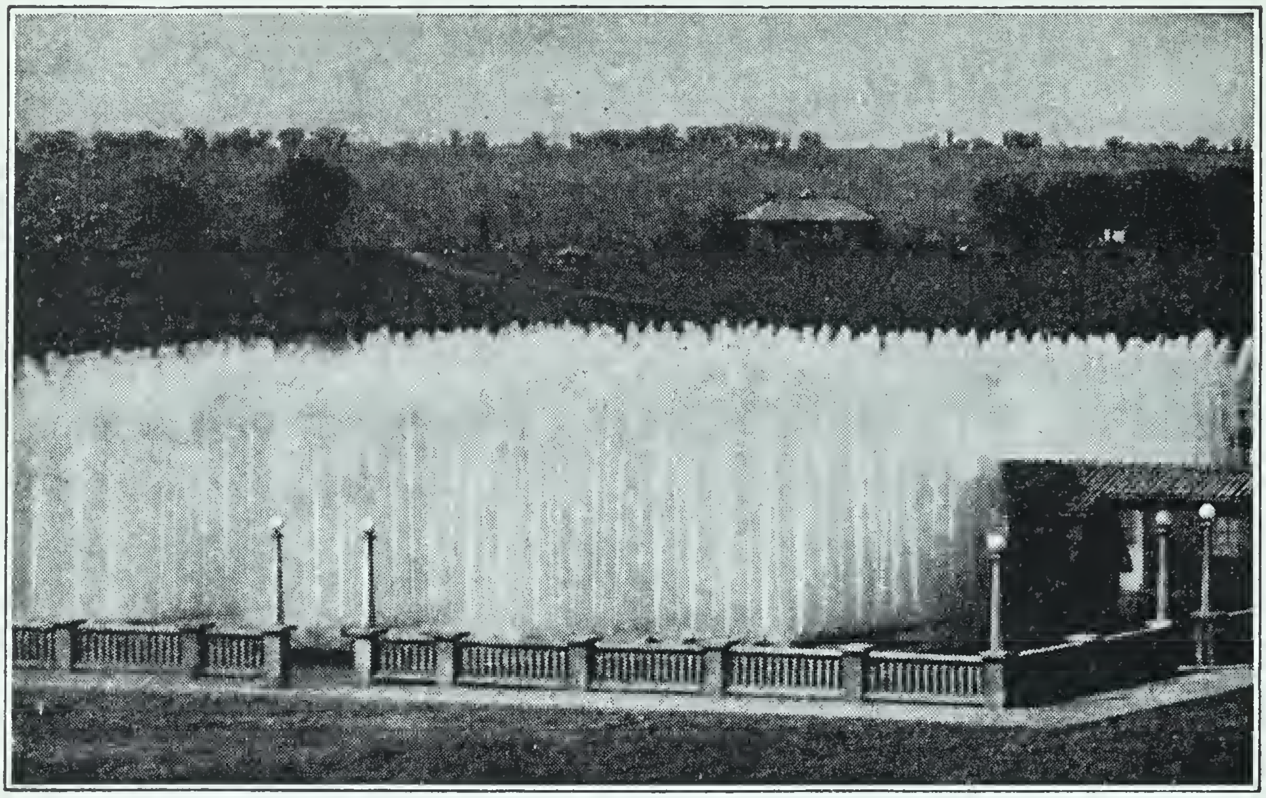
The water problem. Most of us have not known that there is any problem about water, save in some places to get enough of it. This is because there is not much of a problem on farms and in small villages, while in larger towns and cities the problems are solved without our knowing that there have been any.

In thickly settled regions, in cities, and wherever steam boilers are used, there is a threefold problem; the health problem, the laundry problem, and the industrial problem.

Water and the health problem. The only things in any natural water that are at all likely to be injurious to health are *bacteria* (Fig. 82). In scattered places there may be waters poisoned by harmful minerals. Near arsenic deposits there might be poisoned springs. In some places the natural waters contain very small quantities of fluorides, and these have been found to cause a disease of the teeth (especially with children) called "mottled teeth." These conditions are rare.

The danger from bacteria. Practically all natural waters contain bacteria, and the density of bacterial population in a water depends almost wholly on their food supply. Most of these bacteria are harmless or even beneficial, but some species are the direct cause of definite diseases, particularly of typhoid fever (p. 118). These are called disease-causing (pathogenic) bacteria. Apparently they are never found in a really natural water; so any water in a sparsely settled region is likely to be healthful.

As population increases and towns and cities grow, conditions are all changed. Cities and even small towns usually get their water from rivers or lakes, and into them they are apt to empty their sewage. This sewage is likely to contain disease-causing bacteria, coming from diseased persons. It is rich in food for bacteria, and they increase rapidly. Hence water drawn from any lake or stream must be purified to



Ewing Galloway

Fig. 416. Purification of water supplies by aeration

The figure shows the aeration of the water supply of Denver, Colorado. This procedure removes any objectionable gases present and furnishes oxygen to help in the process of purification

prevent disease. This must be done on a large scale; for an average city needs about one hundred gallons daily for each person. The following methods are used:

Aeration of water. Some cities aerate their water supplies by throwing jets of water into the air (Fig. 416). In this way any objectionable gases in the water are removed, while the oxygen helps to oxidize any organic impurities present.

Treatment of water by chlorine alone. Sometimes a water supply is clear and reasonably soft, as is true in New York and in Chicago. All that is needed is to aerate it and then treat it with small quantities of chlorine as it enters the distributing pipes (Fig. 420). This kills the bacteria.

Filtration through slow sand filters, as well as treatment with chlorine. These filters are made of sand and gravel, as shown in Fig. 417. Coarse impurities like mud are strained out. Some organic matter is caught on the filter, and at once bacteria collect on it. In their growth they form a jellylike layer on the surface of the filter, and this takes out both the bacteria and their organic food from the water. For added safety the filtered water is treated with chlorine.

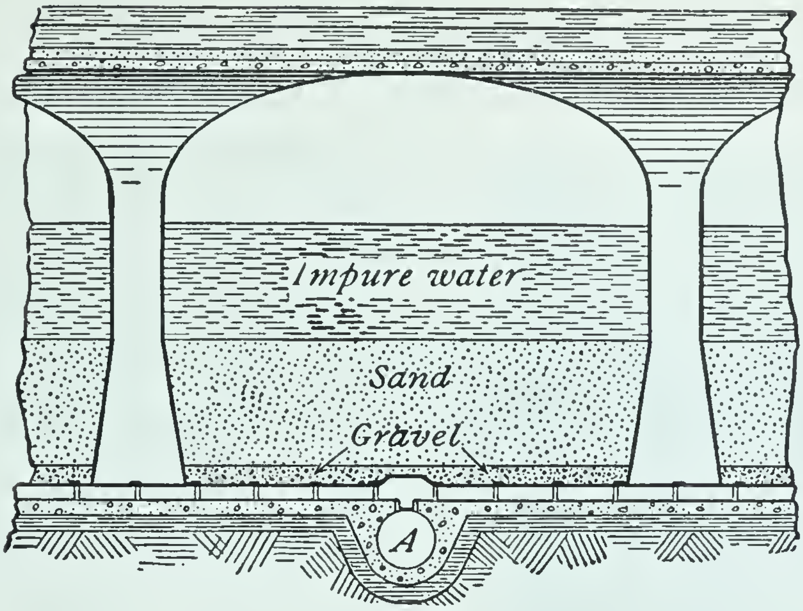


Fig. 417. A covered slow sand filter for purifying water on a large scale

The purified water passes into the porous pipe *A*, from which it is pumped into the city mains

Treatment with aluminum sulfate followed by chlorine. We have seen that aluminum sulfate is readily hydrolyzed in dilute solution, forming colloidal aluminum hydroxide. This slowly coagulates and, as it settles, drags down with it the matter suspended in the water (Fig. 418), including coloring matter and bacteria.

After the precipitate has settled, the (nearly) clear water is drawn off and run through a rapid sand filter *F* (Fig. 419). It is then treated with chlorine.

Water and the domestic problem — hard water. A *hard water* is one that contains a good deal of mineral salts, especially those of calcium and magnesium. These may be in solution as the acid carbonates $Ca(HCO_3)_2$ or $Mg(HCO_3)_2$, or as sulfates or chlorides. It is called "hard" because it uses up soap and feels harsh to the skin.

Water containing the acid carbonates is said to have *temporary hardness*, because it can be softened by boiling. The acid carbonates are decomposed, forming the insoluble normal carbonates (p. 530). But water that has sulfates or chlorides of calcium or magnesium in solution is called *permanently* hard. It cannot be softened by boiling.

How hard water uses up soap. Soap is largely the sodium salt of stearic and palmitic acids (p. 482). Now nearly all other salts of these acids are insoluble in water, including those of calcium and magnesium. So if soap is added to a hard water, the magnesium and the calcium are completely precipitated as stearates and palmitates, in the form of a sticky gum, very familiar in washbasins and bathtubs. The soap used up in this way has no beneficial effect in the laundry and is a dead loss. The sticky gum is hard to wash off the linen in the laundry tubs. So it is important to soften hard water — remove the calcium and magnesium ions — before use in the household.

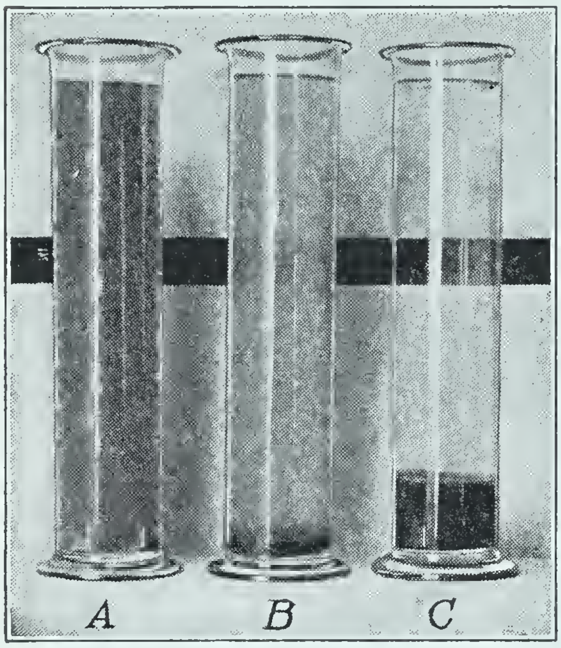


FIG. 418. Purification of water by aluminum sulfate

Cylinder *A* contains impure water before treatment. In cylinder *B* some aluminum sulfate has been added, and the resulting aluminum hydroxide, together with suspended impurities, is slowly settling. In cylinder *C* the settling is complete

How hard waters are softened. In a small way in the home, hard water is often softened by adding a little borax or sodium phosphate. This precipitates the calcium and magnesium as insoluble borates or phosphates, which give little further trouble.

On a large scale, less expensive chemicals are used. The calcium acid carbonate and *all* magnesium ions are removed by adding calcium hydroxide (slaked lime):

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2\,CaCO_3\downarrow + 2\,H_2O$$
$$Mg(HCO_3)_2 + 2\,Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + 2CaCO_3\downarrow + 2\,H_2O$$
$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + CaCl_2$$

The remaining calcium ions are then precipitated by sodium carbonate:

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + Na_2SO_4$$
$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2\,NaCl$$

The insoluble precipitates formed in these reactions settle out as the water slowly flows through *settling basins* (Fig. 421). Aluminum sulfate may be added along with the calcium hy-

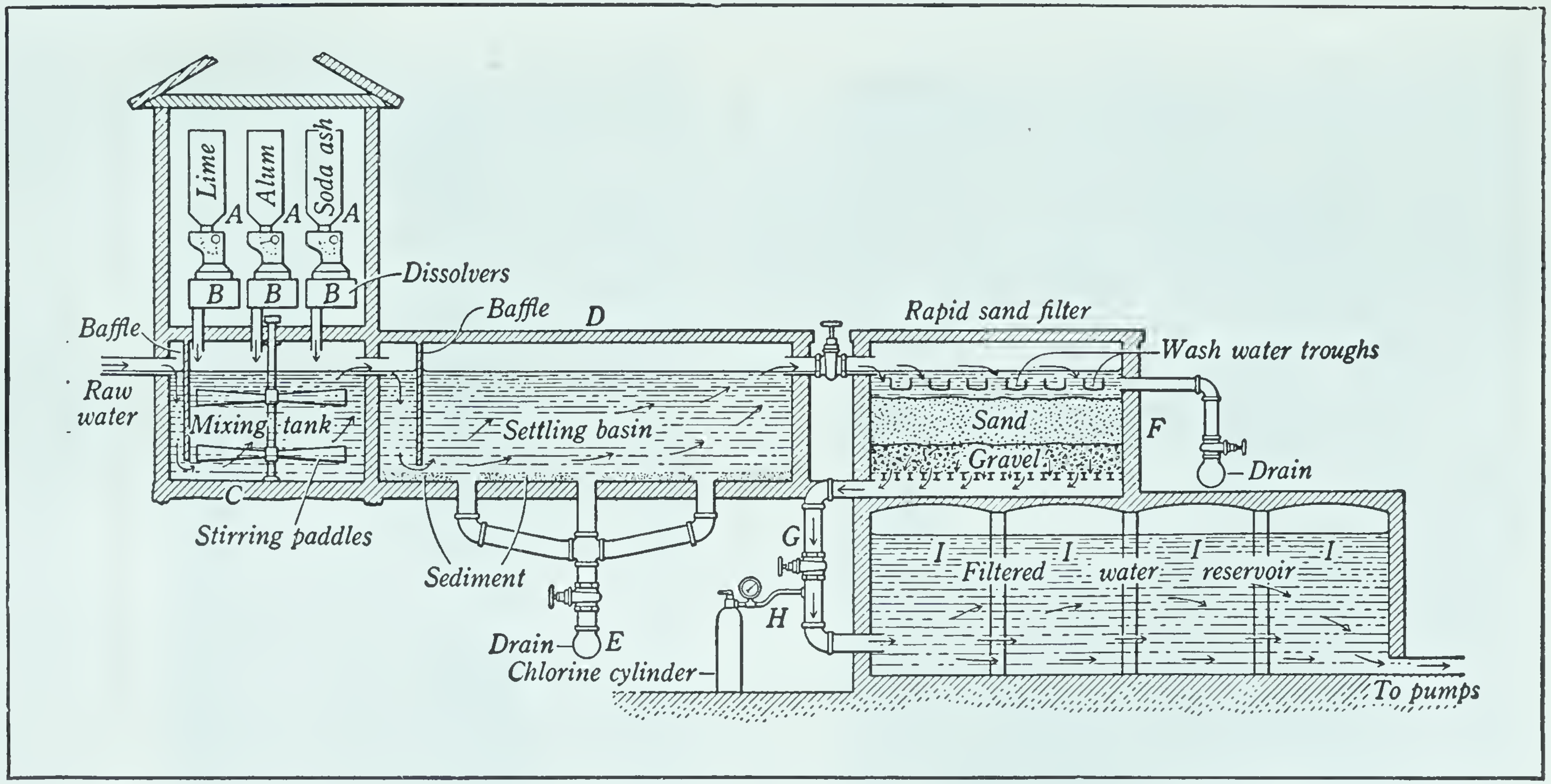

Lime
Alum
Soda ash
A
A
A
B
B
B
Dissolvers
Baffle
Raw water
Mixing tank
C
Stirring paddles
Baffle
D
Settling basin
Sediment
Drain
E
Chlorine cylinder
G
H
Rapid sand filter
Wash water troughs
Sand
Gravel
F
Drain
I
I
I
I
Filtered water reservoir
To pumps

Fig. 419. Diagram showing the essential parts of a plant for purifying and softening the water supply of a city

The impure raw water enters the mixing tank *C*, where it is thoroughly mixed with the purifying and softening reagents entering at the top of the tank, as shown in the diagram. The mixture then flows into the settling basin *D*, where the solids formed by the action of the purifying reagents upon the water settle to the bottom and are drawn off through *E* from time to time. The water next flows through the rapid sand filter *F*, then through the pipe *G* (where the necessary chlorine is added at *H*) into the filtered water reservoir, and from this into the city mains. The rapid sand filters are cleaned by occasionally forcing a stream of water through them in the reverse direction; the water carrying the impurities flows out through the "wash water troughs," as shown in the diagram

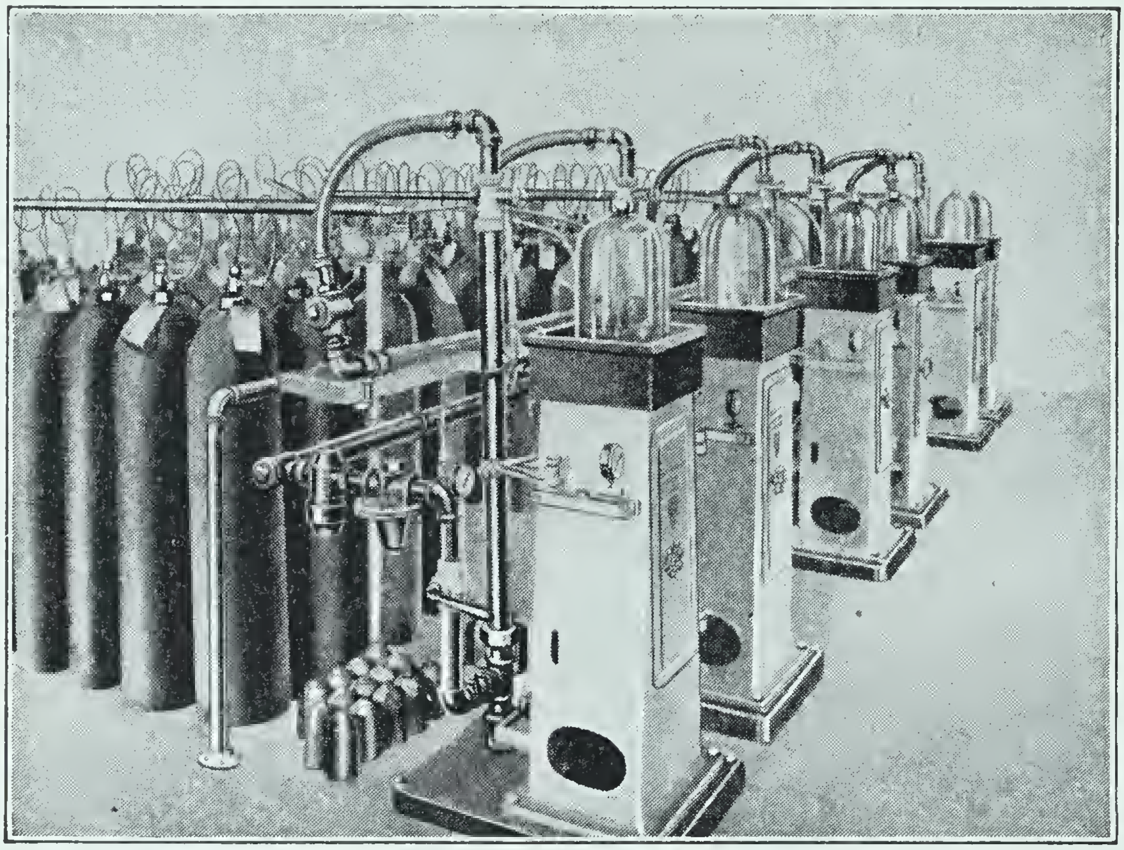


Fig. 420. Water purification by treatment with chlorine

The chlorine is led into the water from the bombs in which it is stored

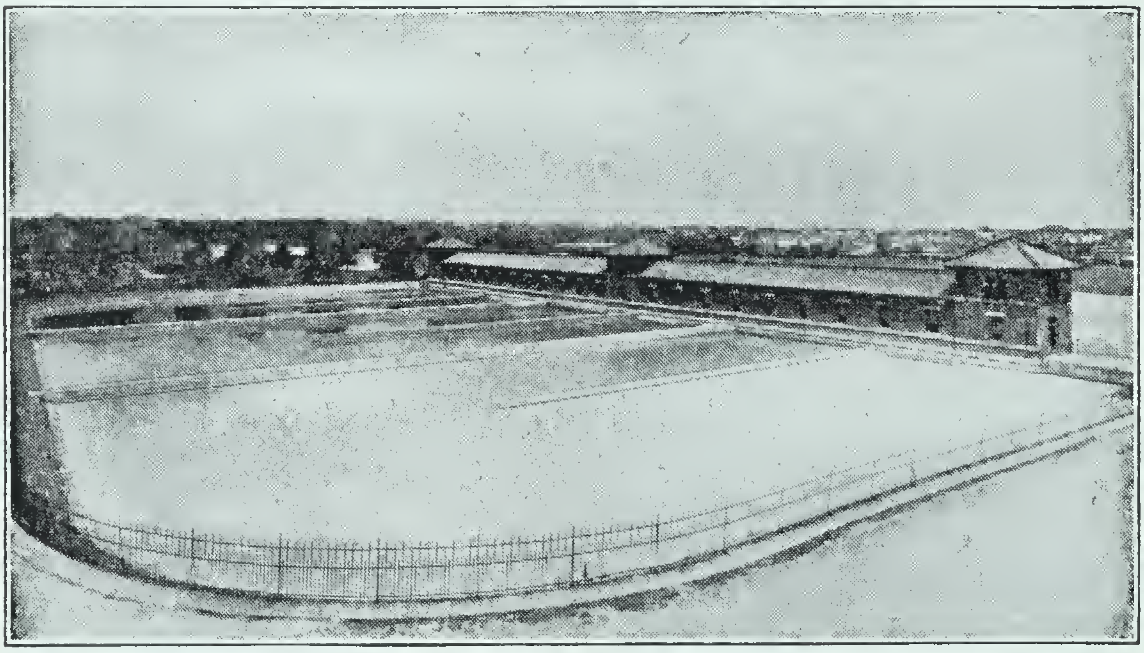
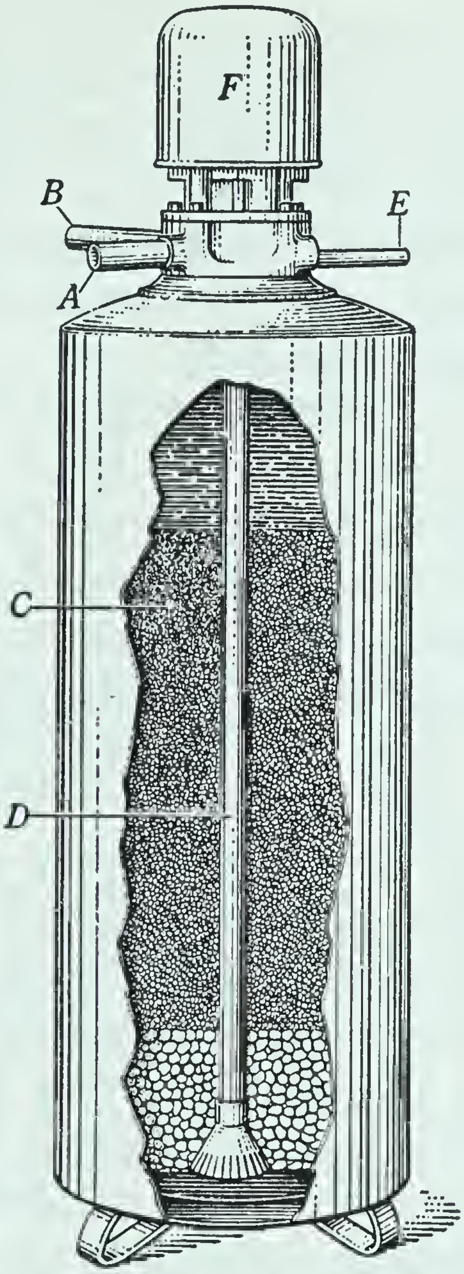


Fig. 421. View of the settling basin at the water works, Columbus, Ohio

The water, mixed with the purifying and softening chemicals, flows into the basin in the foreground and then slowly flows back and forth between the tiers until it reaches the rear of the basin, by which time all the solid materials have settled, leaving the water clear, soft, and pure



The hard water enters at *A* and flows to the bottom of the container through the pipe *D*. It is then forced upward through the zeolite *C*, which removes the calcium and magnesium ions. The resulting soft water flows out through the pipe *B*. From time to time a solution of sodium chloride, forced in at *E*, regenerates the zeolite

FIG. 422. The zeolite process for softening water

droxide and sodium carbonate. The water will then be purified and softened in one operation.

It will be noticed that water treated in this way will contain sodium sulfate and chloride, but these compounds have no effect on soap. Fig. 419 shows how the process of purifying and softening water is carried out on a large scale.

The zeolite process for softening water. The name *zeolite* has been given to a mixture of complex sodium-aluminum silicates found in nature or made artificially. For simplicity we may give them the formula

$$Na_2O \cdot Al_2O_3 \cdot 2\ SiO_2$$

The hard water is allowed to flow slowly through a suitable vessel filled with finely divided zeolite. The calcium and magnesium ions in the water replace the sodium in the insoluble zeolite and are removed from the water, leaving it *soft* water:

$$\begin{aligned} &Na_2O \cdot Al_2O_3 \cdot 2\ SiO_2 + CaCl_2 \\ &\qquad \longrightarrow CaO \cdot Al_2O_3 \cdot 2\ SiO_2 + 2\ NaCl \end{aligned}$$

When the sodium of the zeolite has been largely replaced, a saturated solution of common salt is run through the calcium zeolite, and the original reaction is then reversed by mass action (p. 311). The sodium zeolite so formed is now ready to be used once more (Fig. 422).

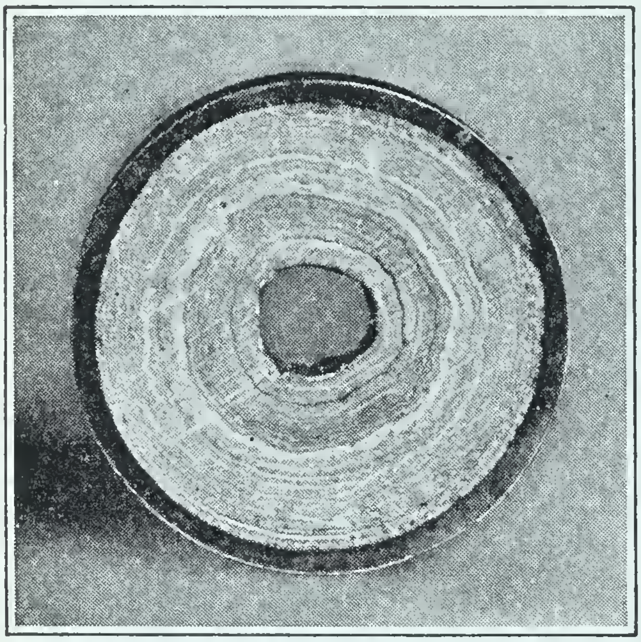


FIG. 423. Deposit of boiler scale inside a water tube of a boiler

Such filters are very convenient in the home in places where the city does not soften the water. Even some towns soften their water supply in this way.

The gain in softening water. The gain in softening city water is very surprising. For example, it is estimated that the softening of the city water of Columbus, Ohio, a city of about three hundred thousand, has made an annual saving in soap alone of $250,000. This does not take into account the money that would otherwise be spent in making cisterns to catch soft rain water, or for small water-softeners for homes and factories. Nor does it cover the great expense due to boiler scale.

The industrial water problem. Every steam engine is driven by steam from water heated in the tubes of a steam boiler. When hard water is used in the boiler, a hard deposit of mineral matter called *boiler scale* is deposited in the boiler tubes (Fig. 423). This material is a poor conductor of heat and so wastes fuel. In time it may almost close the tubes and may make serious trouble. It is very difficult and expensive to remove. All this trouble is avoided by using soft water.

Sewage disposal. It is clear that the problem of safe water is closely connected with the problem of sewage disposal. Every city must provide for safe disposal of its sewage or run the risk of heavy damage suits. The rivers and lakes must be safe for water supply.

Sewage is treated in several ways so that its waste water may be safely returned to the rivers. In some plants it is sprayed into the air until the organic matter has been oxidized and the bacteria greatly reduced in number (Fig. 63). In other cases it is stored for a time in basins. The bacteria destroy the organic matter, and other low forms of life (protozoa) destroy the bacteria. Sometimes what is called *activated sludge* is used to hasten these processes. Before the waste water is returned to the river, it is filtered from all coarse, solid waste, which can then be burned or else used as a fertilizer.

CHAPTER SUMMARY IN QUESTION FORM

1. (*a*) Do we ever find chemically pure water in nature? (*b*) What kinds of impurities are present in natural waters? (*c*) What kind of impurities in our drinking water is injurious to health?

2. Give the different methods used for purifying water on a large scale.

3. (*a*) What is the difference between hard waters and soft waters? (*b*) How can you tell whether a given sample is hard or soft?

4. (*a*) What is the difference between *temporary hardness* and *permanent hardness*? (*b*) To what is each due? (*c*) May the same water have both temporary and permanent hardness?

5. Describe the process by which hard waters are both softened and purified on a large scale.

6. Describe the zeolite process for softening hard waters.

7. What is the advantage gained in softening waters for use (*a*) in our homes? (*b*) for industrial purposes?

8. Describe the different methods used for disposing of sewage.

THOUGHT QUESTIONS

1. What property has chlorine that makes it efficient in water purification?

2. Explain how it is possible to remove calcium compounds from temporary hard water by adding more calcium compounds.

3. (*a*) What is the chemical composition of soap? (*b*) Explain why calcium and magnesium compounds in waters consume so much soap, while compounds of sodium do not.

OPTIONAL EXERCISES

1. Visit the office in charge of the water supply of your city or town, find out the following facts, and report on them: (*a*) source of the water supply; (*b*) whether a gravity or a pumping system is used; (*c*) method of purification used; (*d*) if water is softened, what method is used; (*e*) typhoid-fever rate since water was purified.

2. A certain city uses 30,000,000 gal of water daily, and 100 gal of the water contains 120 g of calcium acid carbonate and 30 g of calcium sulfate. Calculate the weights of calcium hydroxide and sodium carbonate required to soften the daily water supply.

UNIT READINGS

BEERY. *Stuff.* [Chapter XVII tells of sodium, potassium, calcium, barium, and strontium.]

CLARKE. *Marvels of Modern Chemistry.* [Read Chapter XVI, "The Alkali Metals," and Chapter XVIII, "Lime and Magnesia."]

FELSING and POTTER. "Gypsum," *Journal of Chemical Education*, Vol. VII, pp. 2788–2807. [A valuable article.]

FOSTER. *The Romance of Chemistry.* [Read "Natural Waters," pp. 103–108.]

HOBBS. "Some Commercial Applications of Aluminum," *Journal of Chemical Education*, Vol. VII, pp. 245–256.

HOLMES. "The Story of Aluminum," *Journal of Chemical Education*, Vol. VII, pp. 233–244. [The student will find this of great interest.]

HOLMES. *Out of the Test Tube.* [Chapter XXXIII, "The Three Light Metals," treats interestingly of aluminum, magnesium, and beryllium.]

HYLER. "The Production of Salt," *Journal of Chemical Education*, Vol. XII, pp. 203–207. [Brief and well illustrated.]

PIGMAN. *A Story of Water.* [A book elementary in character and written in popular style.]

TILDEN. *Chemical Discovery and Invention in the Twentieth Century.* [Read Chapter XVI, "Water and Its Purification"; also Chapter XXVII, "Fixation of Atmospheric Nitrogen."]

WADE. "Man-Made Gems," *Journal of Chemical Education*, Vol. VIII, pp. 1015–1026. [An excellent and well-illustrated article.]

WEEKS. *The Discovery of the Elements.* [Read of the discovery of the important elements discussed in this unit.]

The Science Leaflet. [No. 18 of recent volumes tells of the sodium family; No. 19, of the calcium family; No. 23, of the zinc family; and No. 24, of aluminum.]

Unit Fourteen. The Heavier Metals and How They Serve Us

THERE is much heavy work to be done in the world, and much of it calls for heavy metals. A railway engine must have weight; otherwise its wheels would spin around trying to pull a heavy load. A steam shovel must be heavy to give momentum to its push. A cannon must be heavy; otherwise its recoil would be as dangerous as its shell.

Some of the heavy metals are below hydrogen in the electromotive series and some are above it. With the exception of iron they do not rust to any marked extent and are not very active toward most reagents. They wear well.

The heavy metals have high melting points and are strong and malleable. What should we do without platinum for our crucibles, tungsten for our electric lamps, and wire of copper and iron for our telegraphs and telephones and for the armatures of all our motors and dynamos? How could we get shafts for our machinery and motorcars without the strength of steel of various kinds? How should we get on without lead for our storage batteries? What should we do for coinage without gold and silver and copper and nickel?

The heavy metals were the ones we first used; for they are the easiest to get. They have served us faithfully, and our arts and industries still depend on them.

CHAPTER XLVIII

Iron, Cobalt, and Nickel

[A Well-Known Metal and Two Near Relatives]

TABLE OF THE THREE METALS

NAME OF ELEMENT	ATOMIC NUMBER	DENSITY	MELTING POINT	ELECTRONS IN ORBITS
Iron (Fe)	26	7.86	1535°	2, 8, 14, 2
Cobalt (Co)	27	8.9	1480°	2, 8, 15, 2
Nickel (Ni)	28	8.9	1452°	2, 8, 16, 2

A new kind of periodic family. In the periodic families so far studied the elements are found in a *vertical* column in the periodic table (p. 323). Iron, cobalt, and nickel are a family of very similar metals placed *horizontally* in Group VIII. It should be noticed that there are two other similar families of metals. In atomic structure the three metals are very much alike. We shall want to know more about iron than about the other two metals.

IRON, THE MOST-USED METAL IN THE WORLD

The abundance of iron. Without doubt, oxygen is the most abundant element in this world *as we know* it. This includes the air, the waters, and the crust of the earth at most a few miles in depth. But there are some good reasons for believing that the whole central part of the earth, with a radius of possibly two thousand miles, is largely iron with some nickel. If this is true, then iron is far more abundant than oxygen. Many of the meteorites that fall on the earth are chiefly an alloy of iron with a little nickel.

With the exception of these meteorites (Fig. 424), we do not find free iron in nature. But for at least four thousand years men have known ways to get iron from its ores. So these must be abundant, and easily worked for the metal.

Iron is found in nearly all minerals. Iron is found in large deposits as oxides, sulfides, and carbonate. In small percentages it is present in a great variety of minerals. Indeed,

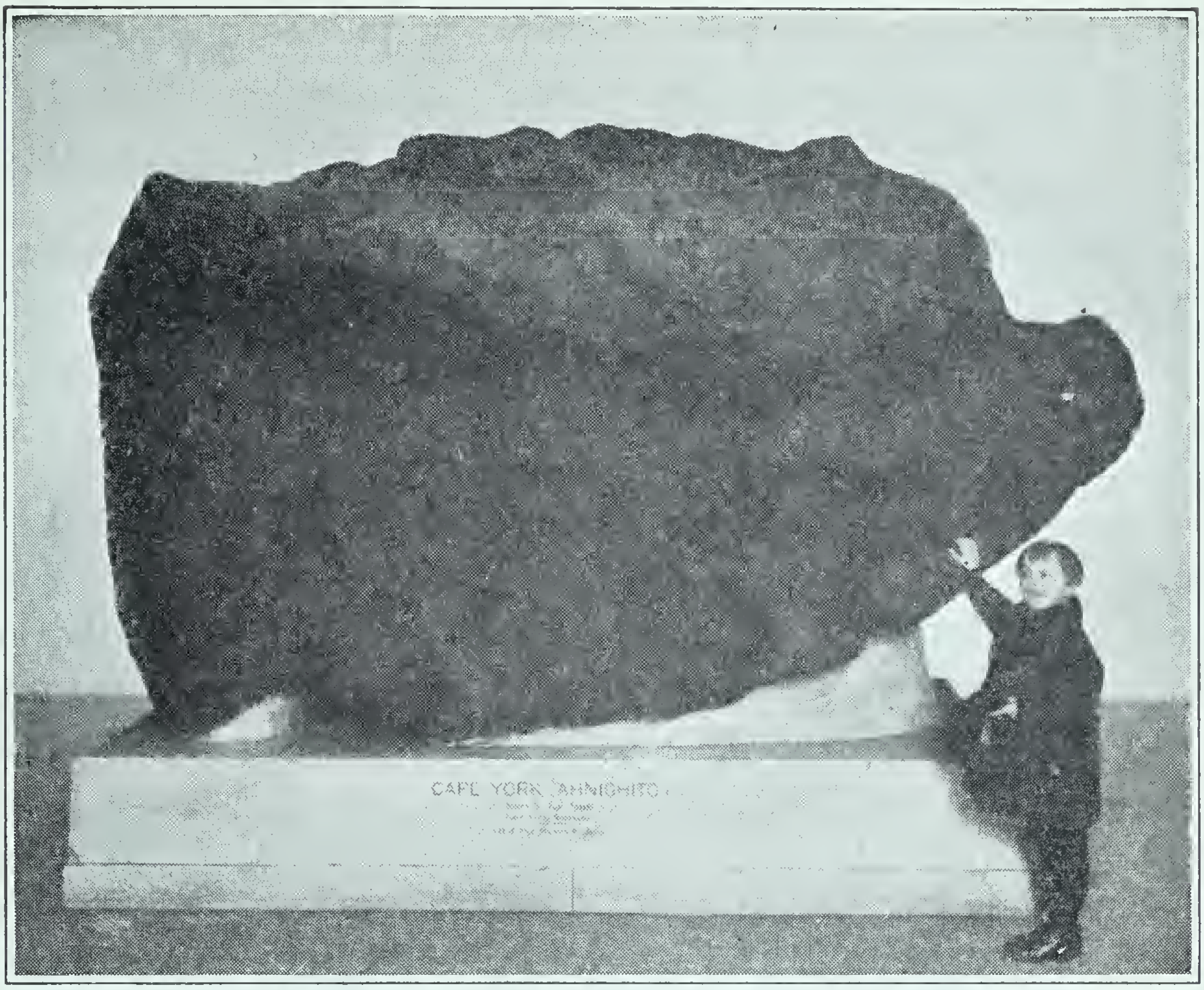


Fig. 424. The Cape York meteorite, discovered by Admiral Peary near Cape York, Greenland, in 1895

It weighs 26½ tons and is made up of iron and nickel. (Courtesy of the American Museum of Natural History)

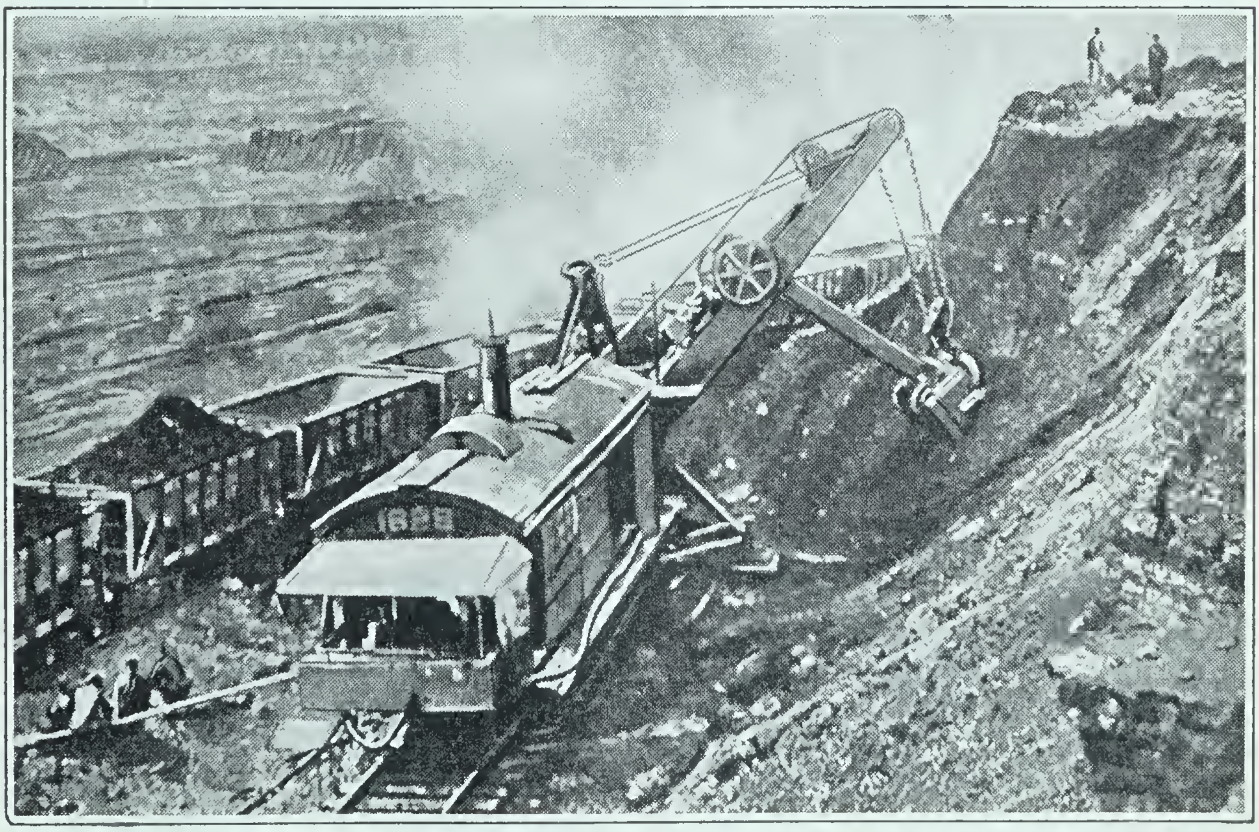


Fig. 425. Mining iron ore in Minnesota — the state that leads all others in the production of this ore

nearly all rocks and soils contain compounds of iron, and their colors are largely due to these compounds. The hemoglobin of the blood of animals contains iron; so our very lives depend on this element.

The iron of commerce. Perfectly pure iron has been made; it is a silvery metal that melts at 1535°. It is ductile and malleable, and is almost as soft as aluminum. Iron with only a few hundredths of 1 per cent of impurities is made on a large scale for certain special purposes.

Even very small percentages of other elements, especially of carbon, bring about great changes in the properties of iron and make it much more useful. So nearly all commercial iron is really an alloy. Carbon is always present in amounts that vary from a mere trace to about 5 per cent. According to the way the iron has been made, the carbon may be present in various forms. It may be as flakes of graphite scattered through the iron; or it may be really dissolved in the iron; or it may form carbides with the iron. Of these carbides the most important has the formula Fe_3C and is called *cementite*. Manganese and silicon, together with traces of phosphorus, sulfur, and oxygen, are usually present.

Kinds of iron. The properties of iron are greatly changed by the percentages of these elements, by their form of combination, and by the heat treatment of the metal while it is being made. As a result there are many kinds of iron. The most common commercial varieties are *cast iron*, *wrought iron*, and *steel*.

The metallurgy of iron. Unlike most of the metals we have studied, iron is made not by electrolysis but by reducing the oxide with carbon:

$$Fe_2O_3 + 3\ C \longrightarrow 2\ Fe + 3\ CO\uparrow$$

This equation is easy to understand, but there are many details in the process. Four kinds of materials are used, as follows:

1. ***Iron ore.*** The ores most frequently used are these:

Hematite	Fe_2O_3	Siderite	$FeCO_3$
Magnetite	Fe_3O_4	Limonite	$2\ Fe_2O_3 \cdot 3\ H_2O$

Iron ore is mined in a number of different localities in the United States, but the greatest center of production is in the neighborhood of Lake Superior (Fig. 425).

2. ***Carbon.*** Carbon in some form is necessary both as a fuel to keep the furnace hot and as a reducing agent. In former times wood charcoal was used for the carbon, but now coke is almost always used.

3. ***Heated air.*** To keep up the high temperature necessary for the reduction of iron ore, a very active combustion of fuel is necessary. This is brought about by forcing a strong blast of air into the lower part of the furnace during the reduction process, the air being *previously heated* to raise the temperature of the combustion.

4. ***Flux.*** All the materials put into the furnace must leave it again, in the form of either gases or liquids. The *iron* is drawn off as the liquid metal after its reduction. The *oxygen* with which it was combined escapes as oxides of carbon. Both the ore and the coke contain *earthy matter* that under ordinary conditions would be left as solid ash and clog the furnace. This material is usually rich in silica and aluminum. To get rid of it, limestone is added along with the ore, and the ash and the limestone together make a high-melting liquid glass. This flows out of the furnace before the heavier iron has been drawn off. The material added, usually limestone, is called the *flux*; the liquid glass is called *slag*.

Cast iron. The first step in the manufacture of any variety of commercial iron is to get *cast iron*, or *pig iron.* The ores are mixed with a suitable flux and are reduced by heating with coke. The chief reaction is

$$Fe_2O_3 + 3\ C \longrightarrow 2\ Fe + 3\ CO \uparrow$$

The reduction is carried out in a large tower called a *blast furnace.*

The blast furnace. The average blast furnace (Fig. 426) is at least 90 feet high and 22 feet in inside diameter at its widest part, narrowing somewhat toward both the top and the bottom. The walls are built of steel and are lined with fire brick. The base is provided with a number of pipes *B*,

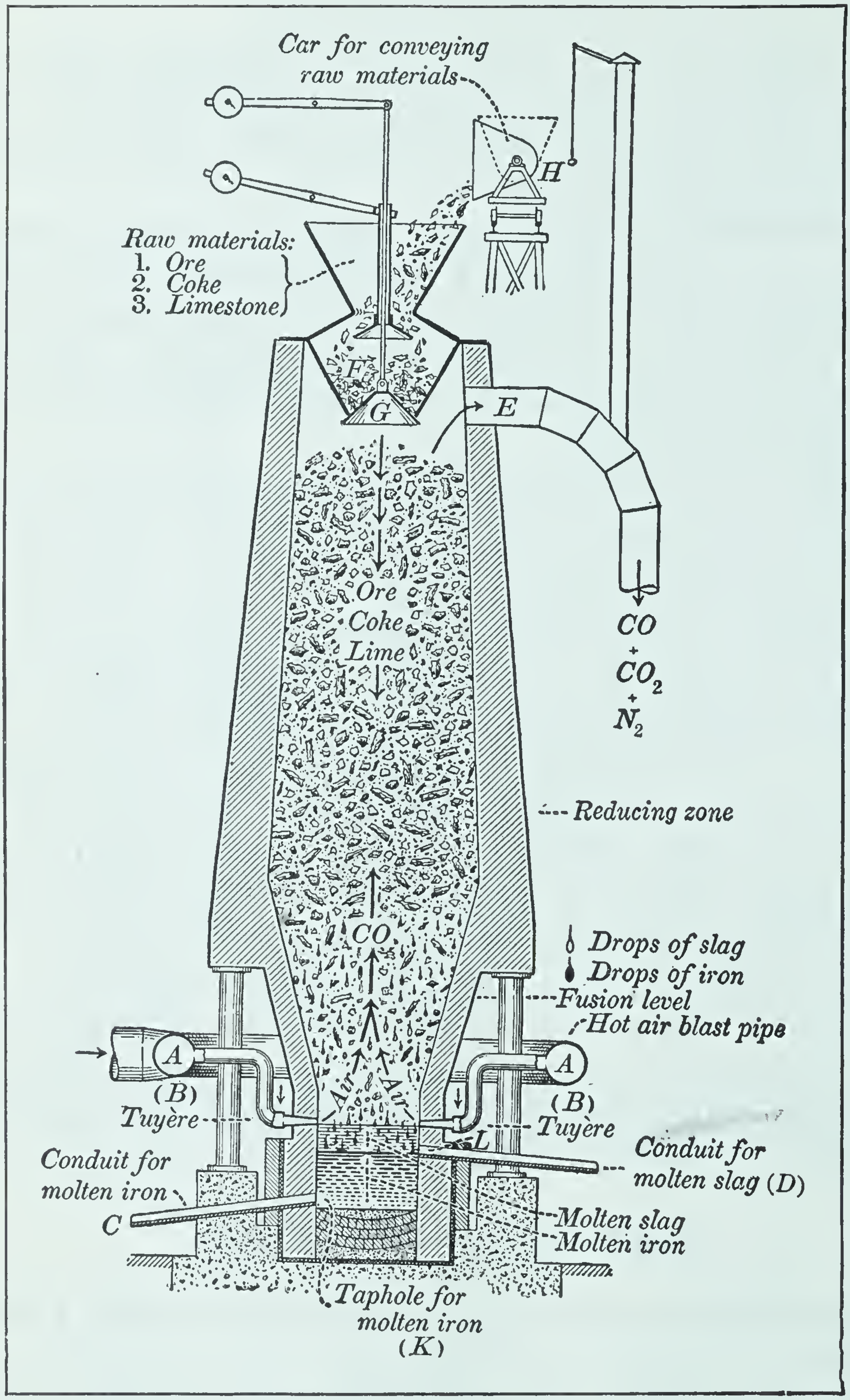

Car for conveying raw materials
H
Raw materials:
1. Ore
2. Coke
3. Limestone
F
G
E
Ore
Coke
Lime
CO
+
CO_2
+
N_2
Reducing zone
CO
Drops of slag
Drops of iron
Fusion level
Hot air blast pipe
A
A
(B)
(B)
Air
Air
Tuyère
Tuyère
L
Conduit for molten slag (D)
Conduit for molten iron
C
Molten slag
Molten iron
Taphole for molten iron (K)

FIG. 426. Vertical section of a typical blast furnace

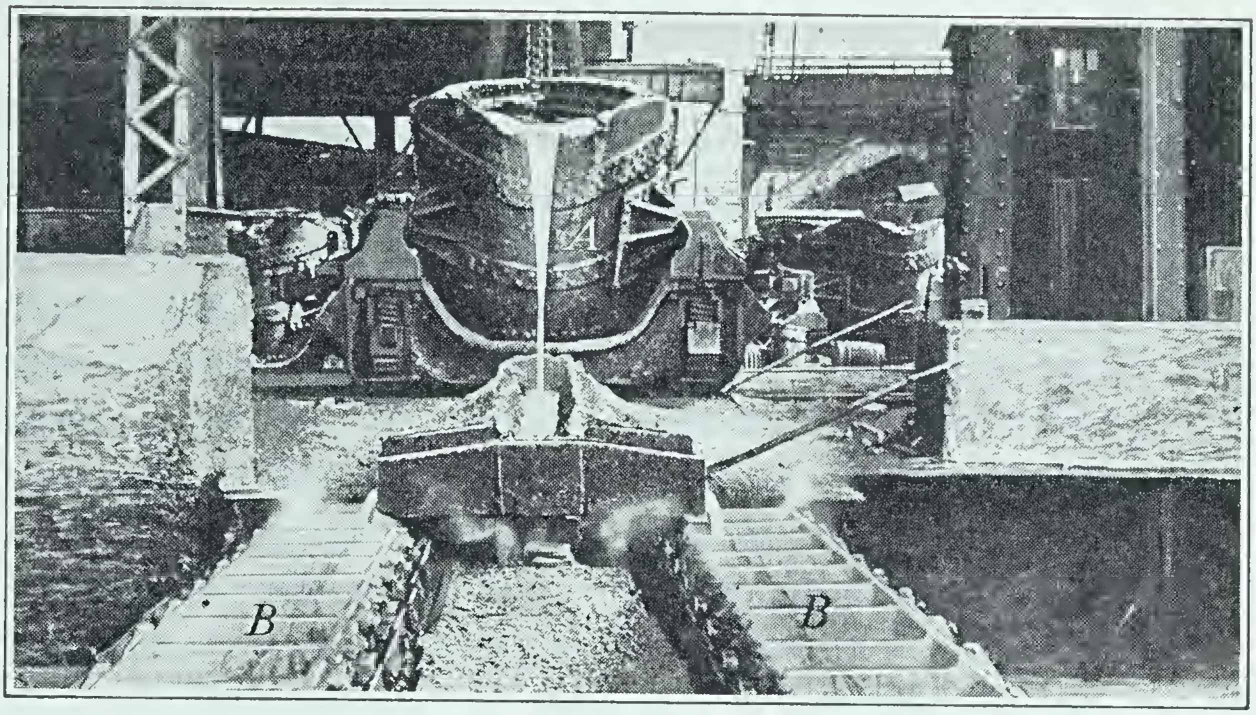


Fig. 427. Casting pig iron from a blast furnace

Liquid iron is poured from the ladles into iron troughs *B*, *B*, or molds lined with lime. These troughs are attached so as to form an endless belt. The molten iron in each trough solidifies by the time it reaches the farthest point; and as the belt reverses, the solid pieces of iron fall into cars placed beneath it

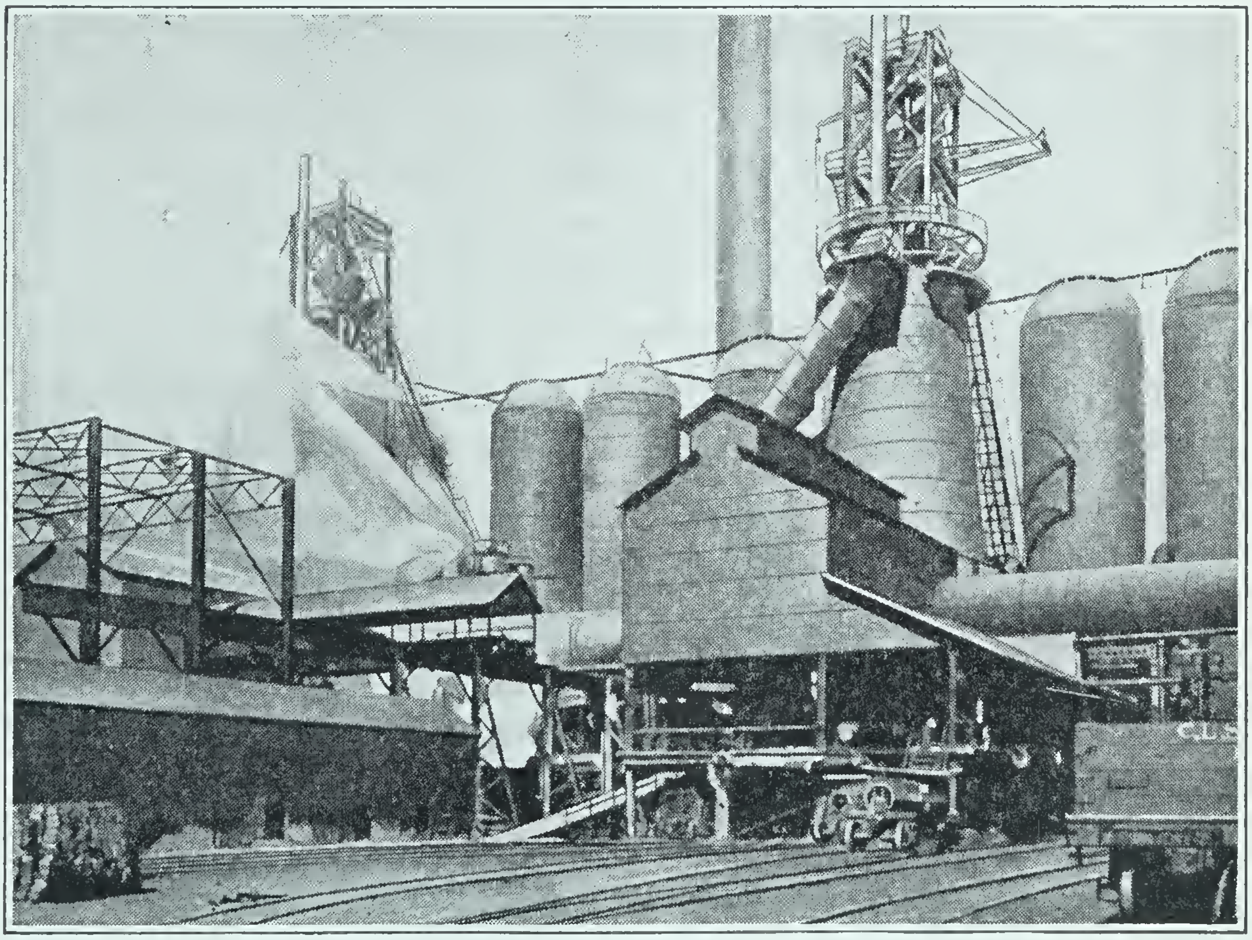


Fig. 428. Exterior view of a blast furnace

In the background is a row of furnaces used for heating the air admitted to the blast furnace called *tuyères*, through which hot air is forced into the furnace. The tuyères are supplied from a large pipe *A*, which girdles the furnace. At the base of the furnace is an opening *C*, through which the liquid metal can be drawn off from time to time. There is also a second opening *D*, somewhat above the first, through which the excess of slag overflows. The top is closed by a movable trap *G*, called the *bell*, and through this the materials to be used are put in. The gases formed by the burning fuel and the reduction of the ore, together with the nitrogen of the air forced in through the tuyères, leave the furnace through the pipe *E*. These gases are very hot and contain enough carbon monoxide to make them combustible; so they are used for heating the blast of air forced in through the tuyères, and as fuel for the engines.

Charging the furnace. Charges consisting of coke, ore, and flux in the right proportion are at intervals dumped into the furnace through the bell. At the bottom of the furnace the coke burns fiercely in the hot-air blast, forming carbon dioxide, which is at once reduced to carbon monoxide as it passes upward through the highly heated carbon.

Reduction of the ore. Reduction of the ore begins at the top of the furnace (the coolest part) through the action of the carbon monoxide on the iron ore. As the ore slowly works down in the furnace the reduction is completed, and the resulting iron melts and collects as a liquid in the bottom of the furnace, under the lighter slag. After enough iron has collected, the slag is drawn off through *D*, and the iron through *C*. The molten iron is then run into large ladles (Fig. 427, *A*), and is either used directly in the manufacture of steel or cast into ingots called *pigs*.

A number of furnaces are usually operated together, as pictured in Fig. 428, which shows an outside view of a modern plant for making cast iron.

What cast iron is like. The iron made in a blast furnace is called *cast iron*. It varies a good deal in composition, but always contains over 2 per cent of carbon, variable amounts of manganese and silicon, and at least traces of sulfur, together with all the phosphorus originally present in the ore and coke. The form in which the carbon is present, whether free or combined, greatly modifies the properties of the iron. In general, cast iron is hard and brittle, and melts at about 1100°. It cannot be welded or forged, but is easily cast in sand molds. It is rigid, but not elastic, and it has little tensile strength.

Wrought iron. Wrought iron is made from cast iron by burning out most of the carbon, silicon, phosphorus, and sulfur, the operation being conducted in what is called a *puddling furnace.*

Wrought iron is soft, malleable, and ductile. Its tensile strength is greater than that of cast iron, but less than that of most steel. Its melting point is much higher than that of cast iron. It is no longer made to the same relative extent as it used to be, because soft steel is cheaper and has almost the same properties.

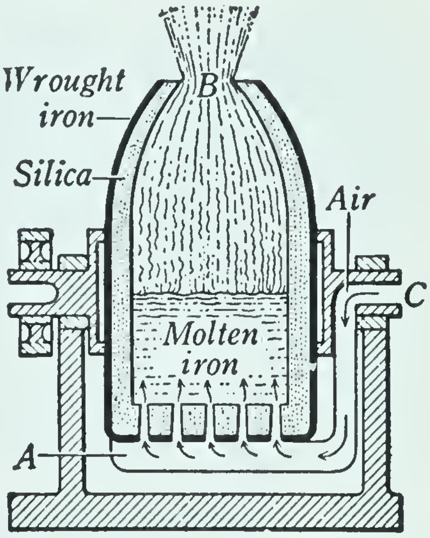


Fig. 429. Vertical section of a Bessemer converter

Steel. Steel, like wrought iron, is made from cast iron by burning out a part of the carbon, silicon, phosphorus, and sulfur, but the processes used are entirely different. In the United States nearly all the steel of commerce is made by one of two general methods: the *acid Bessemer process* and the *basic open-hearth process.*

Acid Bessemer process. In the acid Bessemer process the furnaces used are called *converters* (Figs. 429 and 430). These are lined with *silica*, which, it will be recalled, is an *acid anhydride*; hence the term *acid process.* These furnaces remove the carbon and silicon from the cast iron, but not the phosphorus and sulfur. *The process is therefore used when the cast iron is low in phosphorus and sulfur.*

The Bessemer converter. The Bessemer process, invented about 1860, is carried out in great egg-shaped converters (Fig. 429), one of which often holds as much as 25 tons of steel. The converter is built of iron and, as noted above, is lined with silica. It is mounted on axles, or *trunnions*, so that it can be tipped over on its side for filling and emptying. One of the trunnions, *C*, is hollow, and a pipe connects it with an air chamber *A*, which forms a false bottom to the converter. The true bottom is perforated so that air can be forced into the converter through the trunnion and the air chamber.

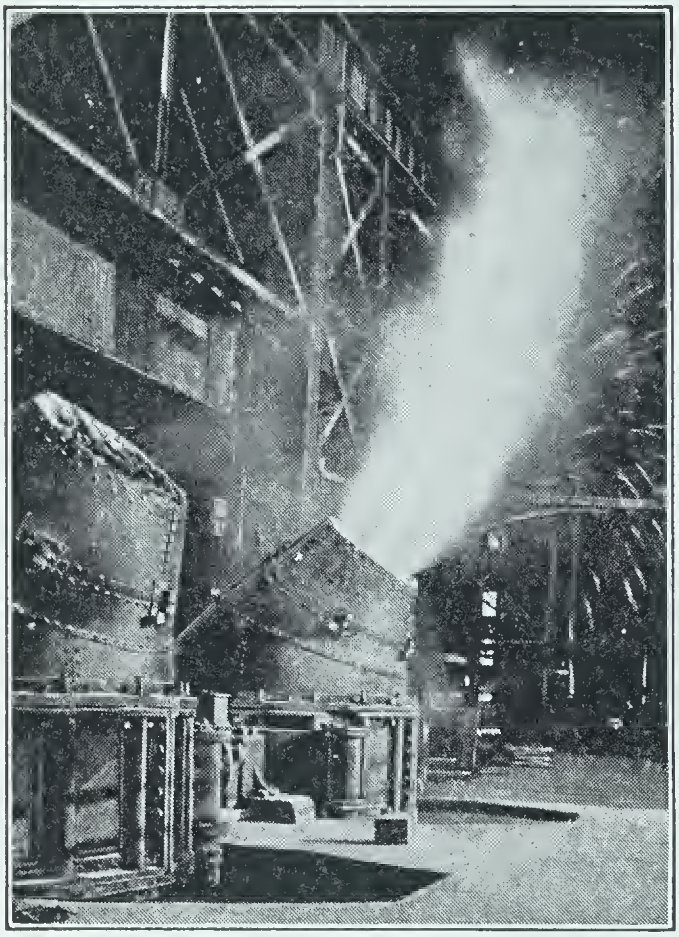


FIG. 430. The brilliant flame of a Bessemer converter

The Bessemer process: how it works. White-hot liquid cast iron from a blast furnace is run into the converter through its open necklike top, *B*, the converter being tipped over to receive it. The air blast is then turned on and the converter moved on its trunnions into a nearly vertical position. The carbon and silicon in the iron are rapidly oxidized (first the silicon and after that the carbon). Brilliant flames and showers of sparks come out of the neck of the converter during this oxidation (Fig. 430). The heat of the reaction, largely due to the combustion of silicon, keeps the iron melted. The air blast is kept up until the look of the flame shows that all the carbon has been burned away.

The process requires from fifteen to twenty minutes; and when it is complete, the desired quantity of carbon (in the form of high-carbon iron alloy) is added and allowed to mix thoroughly with the liquid iron. The converter is then tilted and the steel run into molds (*D*, Fig. 433) to solidify. The resulting masses, known as ingots, are then hammered or rolled into rails or other objects.

Basic open-hearth process. If there are more than traces of phosphorus and sulfur in finished steel, the metal is so brittle that it is worthless for most purposes. In the basic open-hearth process (Fig. 431), in which the lining of the furnace is made of *limestone* or *dolomite*, both of which act as

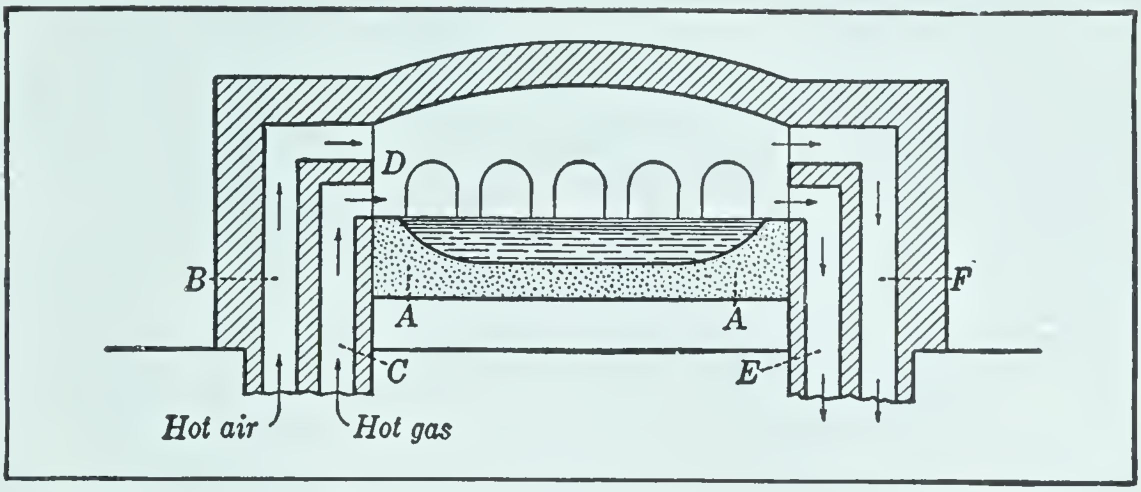


Fig. 431. Diagram of an open-hearth furnace

The fuel gas previously heated enters through C, and at D meets a current of hot air entering through B. The hot flame passes over the cast iron in the furnace, melting it and changing it into steel. The hot products of combustion escape through E and F and are used in heating the incoming supplies of gas and air. The limestone lining is shown at A, A

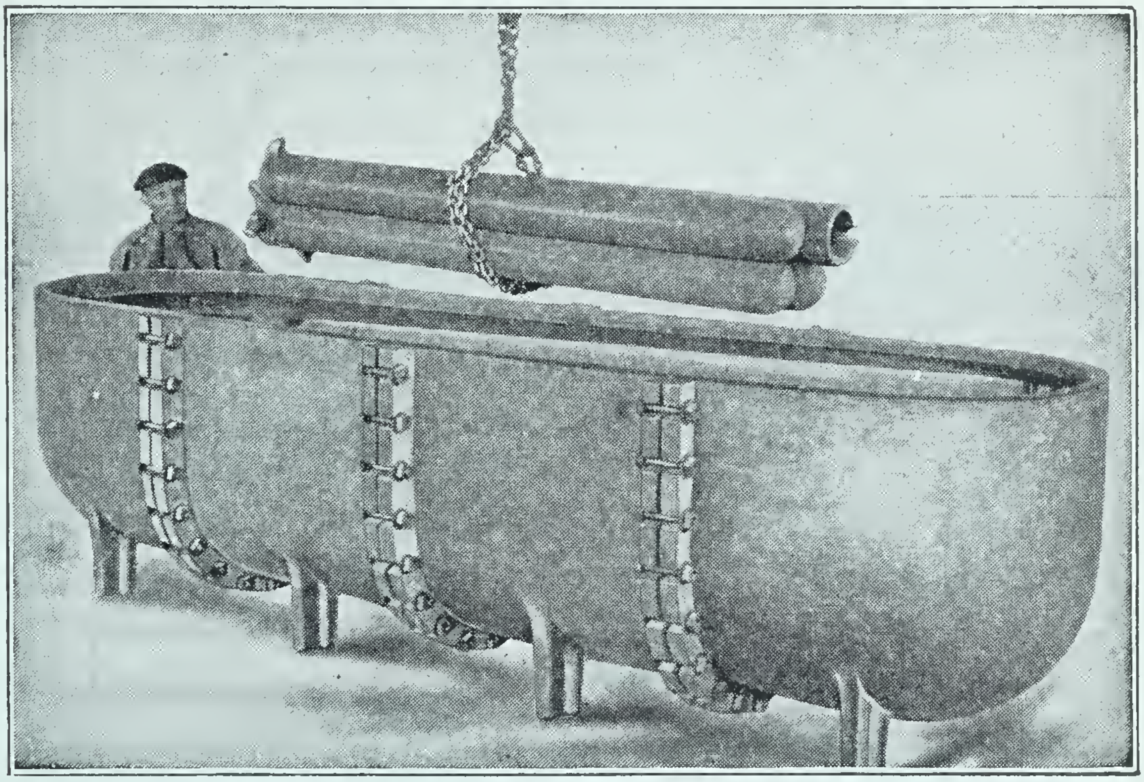


Fig. 432. Cleaning the surface of iron pipes

In the figure there are shown a number of iron objects about to be lowered into a bath of sulfuric acid in order to clean the surface of the iron, since this element, as well as its oxides, is readily attacked by the acid. The bath containing the sulfuric acid is also made of iron, but along with the iron is a certain amount of silicon, these two elements forming an alloy called *duriron*, which is only very slightly attacked by acids

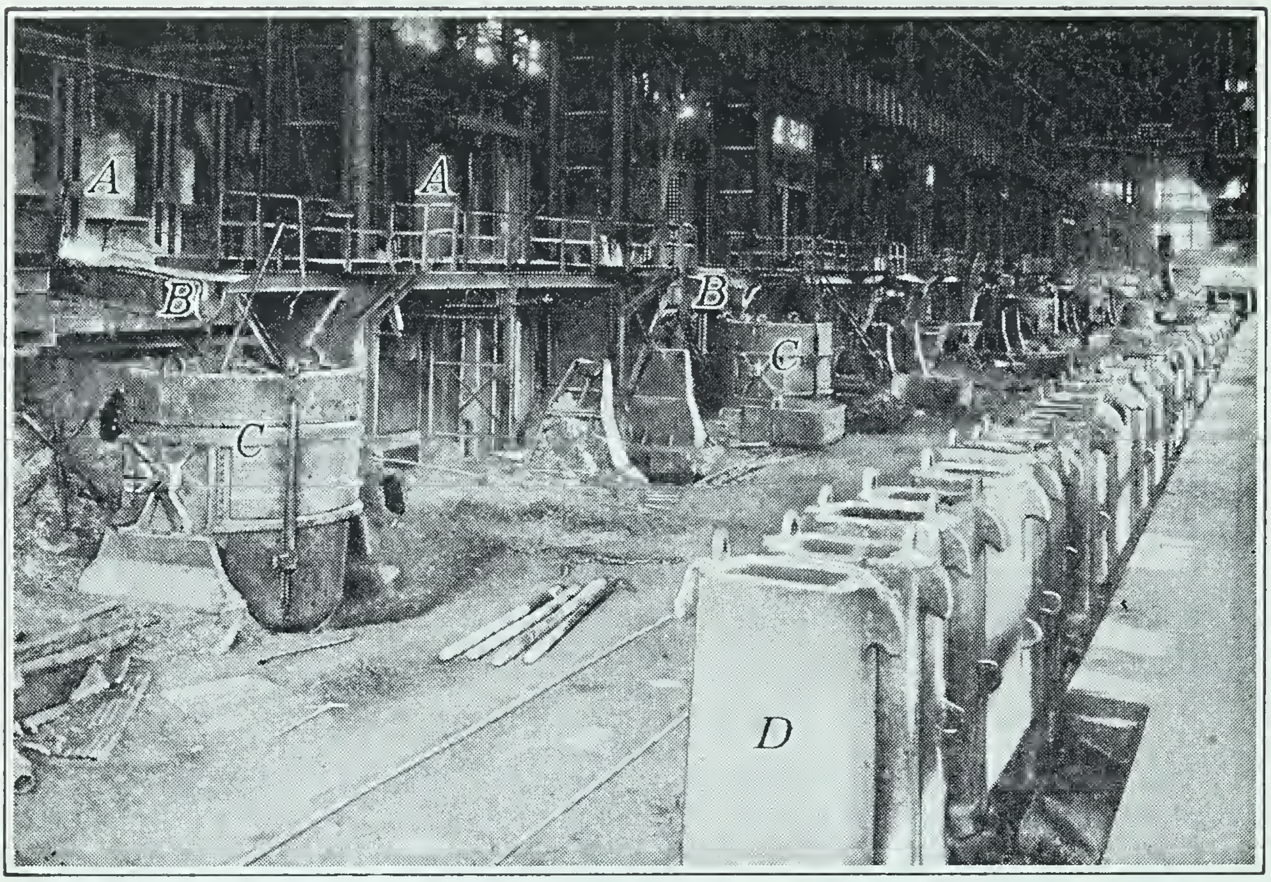


Fig. 433. Casting open-hearth steel

The molten steel flows from the furnaces A, A, down the troughs B, B, into the buckets C, C. It is then poured into the molds D, where it solidifies. The blocks of steel so obtained are known as ingots

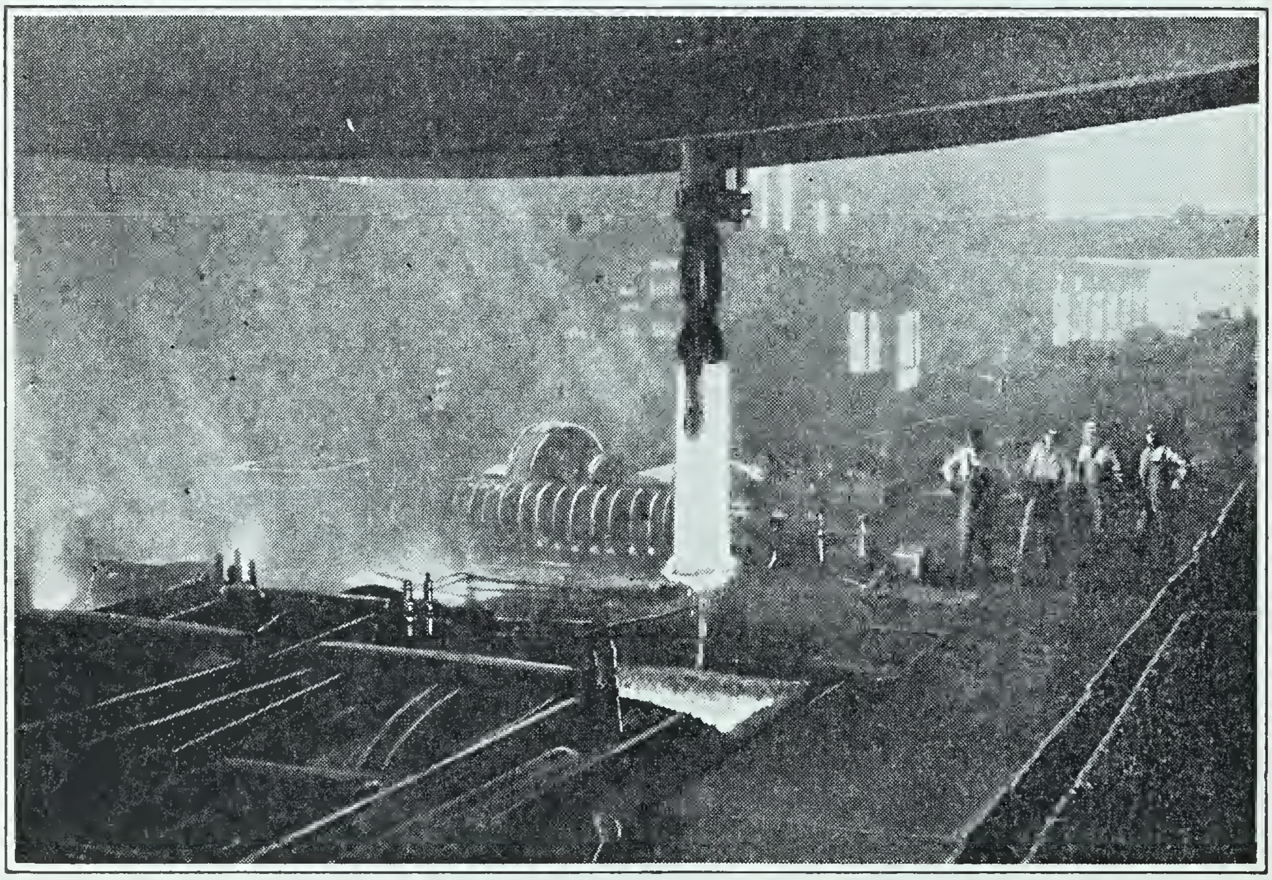


Fig. 434. Hot steel ingot ready for rolling

The ingots are heated white-hot and carried by traveling cranes to the rolling mill to be rolled into sheets or rails *bases*, the phosphorus and sulfur are both removed, as well as the silicon and carbon.

The cast iron is converted into steel by heating it in long furnaces (Fig. 431) with a gas flame that is reflected by the roof of the furnace upon the surface of the iron. Such a furnace is called a *reverberatory* furnace, because the heat is reflected downward by the roof. Flames from sprayed oil or finely powdered coal are also used.

The carbon in the iron is oxidized, and escapes as gas. The silicon, phosphorus, and sulfur are also oxidized, and the resulting oxides combine with some of the basic lining to form a slag. This floats on the surface of the steel and is easily removed. When the operation is complete, the liquid steel is drawn off and cast into ingots (Figs. 433, 434). Most of our steel is made by this process.

Properties of steel. Steel contains from a trace up to 2 per cent of carbon, less than 0.1 per cent of silicon, a little manganese, and not more than traces of phosphorus and sulfur. When desired, a steel containing as high as 99.85 per cent of iron can be made by the open-hearth method. Such steel is very soft, but does not rust easily. As the percentage of carbon increases, the steel becomes harder and less ductile. Steel can be rolled into sheets, cast in molds, and forged into desired shapes.

The hardening and tempering of steel. Steel containing from 0.5 to 1.5 per cent of carbon can be made very hard and brittle. This is done by heating it to a relatively high temperature and then suddenly cooling it by plunging it into cold water or oil. When this hardened steel is gradually reheated and then allowed to cool slowly, it becomes softer and less brittle. This process is known as *tempering*.

By regulating the temperature to which the steel is reheated in tempering, it is possible to obtain any degree of hardness suited to a given purpose.

Alloys of iron. Many different elements (chiefly metals) form useful alloys with iron. It follows that the number of these alloys is very large. The automobile industry alone specifies over seventy of them (Fig. 381) and uses more than any other industry.

Since each of the alloy elements added to the iron gives to it certain properties, depending upon the element added, by making the right selection we may obtain an alloy having almost any desired properties. Thus we may make an alloy that is hard, but not brittle; or one that is elastic or tough; or one that will not rust. For many uses, steel must have great tensile strength, as in piano wires and bridge materials. For example, in the construction of the Oakland–San Francisco Bridge (Fig. 166) there were used 200,000 tons of steel alloyed with nickel and manganese — metals that give great tensile strength to steel.

Many of the alloys have special trade names. For example, the one that contains from 12 to 15 per cent of silicon and is acid-resisting (Fig. 432) is known as *duriron*. Sometimes alloys of various compositions are grouped together according to their similar properties. Thus the term *stainless steel* includes a number of alloys of iron, all containing chromium, and some containing nickel in addition (Fig. 453).

COMPOUNDS OF IRON

Metal ions with two valences. The atoms of each of the metals so far studied have but *one* valence — either 1, 2, or 3. The atoms of iron can give up *either* 2 or 3 valence electrons, forming the *ferrous* ion Fe^{++} or the *ferric* ion Fe^{+++}. In ferrous salts, such as $Fe^{++}Cl^{-}_2$, iron is bivalent, and these are like zinc salts in formulas and in many properties. In ferric salts, like $Fe^{+++}Cl^{-}_3$, iron is trivalent, and these are like salts of aluminum in their formulas.

Most of the metals we have yet to study have two valences or even more. So they form many kinds of compounds.

Ferrous salts. We can get soluble ferrous salts by dissolving iron in the right acid. When crystallized from water they are usually hydrated and are green in color. The insoluble ones can be made by precipitation.

Ferrous sulfate ($FeSO_4 \cdot 7\ H_2O$) (green vitriol, or copperas). This salt is a by-product in the steel-plate mills. When iron is to be galvanized (p. 544) or tinned, its surface must be cleaned from rust and scale with dilute sulfuric acid.

In doing this some of the iron dissolves, and from the resulting solution green vitriol crystallizes. It is used for making blue pigments (Prussian blue), for purifying water instead of aluminum sulfate, and for making black inks (p. 585).

Ferrous chloride ($FeCl_2 \cdot 4\ H_2O$). This salt is well crystallized and is green in color.

Ferric salts. Crystallized ferric salts are usually yellow or violet in color. Heated in solution, they hydrolyze even more easily than salts of aluminum, giving colloidal dispersions of hydrated ferric oxide, $Fe_2O_3 \cdot xH_2O$.

Ferric chloride ($FeCl_3 \cdot 6\ H_2O$). This is the best-known ferric salt. It can be made by dissolving iron in hydrochloric acid and then passing chlorine into the solution:

$$Fe + 2\ HCl \longrightarrow FeCl_2 + H_2\uparrow$$
$$2\ FeCl_2 + Cl_2 \longrightarrow 2\ FeCl_3$$

A more general way, which can be used for all ferric salts, is to treat an *acid solution* of the ferrous salt with an oxidizing agent:

$$2\ FeCl_2 + 2\ HCl + O \longrightarrow 2\ FeCl_3 + H_2O$$

Ferric sulfate ($Fe_2(SO_4)_3$). Ferric sulfate is made from ferrous sulfate by the use of an oxidizing agent:

$$2\ FeSO_4 + H_2SO_4 + O \longrightarrow Fe_2(SO_4)_3 + H_2O$$

Like aluminum sulfate, it forms a series of alums.

Oxidation and reduction of iron salts. Let us write in ionic form the equation for making ferric chloride, also that for making ferrous chloride:

$$2\ Fe^{++}, Cl^{-}{}_2 + Cl_2 \longrightarrow 2\ Fe^{+++}, Cl^{-}{}_3 \qquad (1)$$
$$Fe^{+++}, Cl^{-}{}_3 + H \longrightarrow Fe^{++}, Cl^{-}{}_2 + H^{+}, Cl^{-} \qquad (2)$$

We have learned (p. 207) that oxidation consists in losing one or more electrons, while reduction consists in capturing them. In equation (1) above, the iron ion Fe^{++} loses an electron, becoming Fe^{+++}, and we say it has been oxidized. In equation (2), on the other hand, the iron ion Fe^{+++} captures an electron, becoming Fe^{++}, and so has been reduced.

Hydroxides and oxides of iron. A soluble base ($NaOH$) added to a solution of a ferrous salt gives a white precipitate of insoluble *ferrous hydroxide* ($Fe(OH)_2$). This is oxidized very fast by air and water to ferric hydroxide.

Ferric hydroxide ($Fe(OH)_3$) is at once precipitated as a rusty-red colloidal substance when a soluble base is added to a solution of a ferric salt:

$$FeCl_3 + 3\ NaOH \longrightarrow Fe(OH)_3\downarrow + 3\ NaCl$$

When heated, ferric hydroxide loses water and is changed into *ferric oxide* (Fe_2O_3). This is by far the most important oxide of iron, and is found in large deposits in nature as hematite. *Magnetic oxide* of iron has the formula Fe_3O_4.

Rusting of iron. Ordinary iron is changed by water and air into reddish-brown rust, which has the composition of the mineral limonite ($2\ Fe_2O_3 \cdot 3\ H_2O$). The iron is first *oxidized* by water to ferrous hydroxide, the hydrogen of water being *reduced* to free hydrogen:

$$Fe + 2\ H_2O \longrightarrow Fe^{++}, (OH^-)_2\downarrow + H_2$$

The ferrous hydroxide is then oxidized by air to form rust:

$$4\ Fe(OH)_2 + O_2 \longrightarrow 2\ Fe_2O_3 \cdot 3\ H_2O + H_2O$$

Rust is porous, so the action of water eats deep into the iron. Very pure iron rusts slowly, but alloy material in the iron often hastens rusting. Other alloys, such as stainless steel, do not rust at all. The nation's annual rust bill is an enormous sum of money.

Sulfides of iron. *Ferrous sulfide* (FeS) is found in nature as the mineral pyrrhotite. It is easily made by heating iron with sulfur and is used for getting hydrogen sulfide (p. 353). Iron disulfide (FeS_2) is a very abundant brass-yellow mineral, and is called *pyrite* or *fool's gold.* It is burned to get sulfur dioxide for making sulfuric acid.

Sodium ferrocyanide ($Na_4Fe(CN)_6$); potassium ferrocyanide ($K_4Fe(CN)_6$). These are the sodium and the potassium salt of the acid $H_4Fe(CN)_6$, and are made from by-products in the manufacture of coal gas. They are soluble yellow solids, and the potassium salt is often called *yellow prussiate of* *potash.* When a solution of either is added to a solution of a *ferric* salt such as ferric chloride, a deep-blue precipitate of ferric ferrocyanide forms. This is called *Prussian blue.* It is used as a paint pigment and sometimes for bluing laundry water. This blue precipitate is a good test for Fe^{+++} ions.

Potassium ferricyanide ($K_3Fe(CN)_6$). By treating a solution of potassium ferrocyanide with chlorine water and evaporating the solution to crystallization, garnet-red crystals are formed of the composition $K_3Fe(CN)_6$:

$$2\ K_4Fe(CN)_6 + Cl_2 \longrightarrow 2\ K_3Fe(CN)_6 + 2\ KCl$$

When a solution of ferricyanide is added to a solution of a *ferrous* salt, a blue precipitate (Turnbull's blue) is formed, which is a good test for Fe^{++} ions.

Blueprinting. When a ferric salt and potassium ferricyanide are brought together in solution, no precipitate forms, though the solution becomes yellowish in color. In the sunlight the ferric salt is partially reduced to ferrous salt, and a blue precipitate forms. The process of *blueprinting* depends upon these facts. A sensitive paper is made by soaking paper in a solution of potassium ferricyanide and a ferric salt (ferric ammonium citrate is generally used), and drying it in a dark place. When a drawing in black ink on tracing cloth is laid on such a sensitive paper and the two are exposed to the sunlight, the sensitive paper (except under the black lines) turns a brownish color. It is then thoroughly washed with water to remove the soluble salts. During the washing the parts acted upon by the light turn blue, while the unaffected parts are left white. A solution of sodium hydroxide can be used as an ink for white lettering on a blueprint, since this base decolorizes the blue compound present.

NICKEL AND COBALT

The twin metals. Nickel and cobalt have nearly the same atomic weight and in many ways are very much alike. As good companions they are often found together in ores which nearly always contain sulfur, arsenic, silver, copper, and often manganese. Canada produces about 85 per cent of the world's nickel and shares the chief production of cobalt with the Belgian Congo. Cobalt is usually a by-product of silver or copper mining.

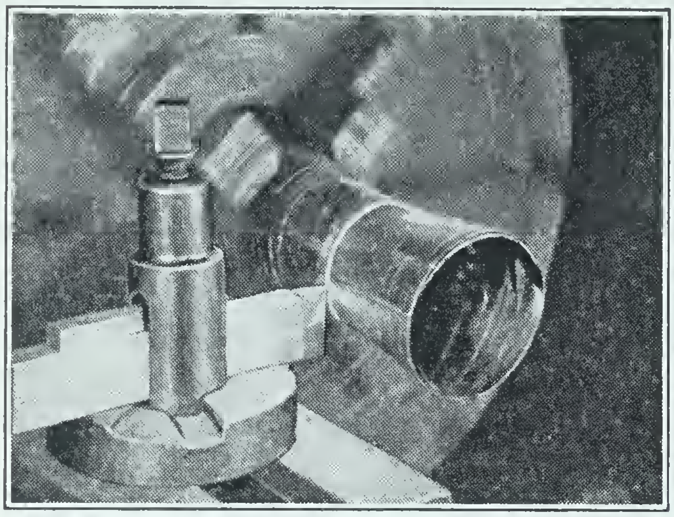


Fig. 435. Carboloy

Cutting a glass tube with a carboloy lathe tool

What the two metals are like. Both metals are silvery in appearance and take a high polish. They are a little heavier than iron, melt at a lower temperature, and do not rust. The chief use of both metals is for plating on other metals (p. 503), and in numerous alloys. In general they add hardness and strength, as well as resistance to vibration and to chemical action (particularly that of alkalies and water).

A sheet of pure nickel is sometimes put on a sheet of steel, and the two sheets are rolled out together. This is called *nickel-clad steel.* Such metal can be pressed or stamped into various forms. Metals like iron are often nickel-plated (Fig. 380). Finely divided nickel is used as a catalyst in many reactions; for example, in the hydrogenation of oils. Cobalt has one curious use. It serves as a binder to hold in place crystals of the very hard tungsten carbide, which then acts as a lathe tool called *carboloy* and is used for cutting very hard substances like hard glass (Fig. 435).

Nickel and cobalt alloys. Nickel is one of the metals in a great number of alloys. *Nickel coinage* is three-fourths copper and one-fourth nickel. *German silver* contains zinc in addition to copper and nickel.

Monel metal is one of the most important of nickel alloys. It is made up of about two thirds nickel and one third copper, and is made directly from copper-nickel ores. It looks like nickel and is used for all sorts of purposes where a metal body is needed that resists rust and corrosion. This includes machinery for making chemicals and drugs, kitchen sinks and table tops (Fig. 382), fixtures for soda fountains and similar fittings. The eight great 297-ton gates that regulate the flow of water from Boulder Dam (Fig. 295) into the hydroelectric plant rest on seats and move on guides which are made of monel metal.

Stellite is a name used for very hard chromium-cobalt alloys which usually have, in addition, either tungsten or molybdenum. They are used for lathe tools that can be handled even at a red heat without losing temper.

Compounds of nickel and cobalt. These compounds are less important than the metals themselves. *Nickel sulfate,* $NiSO_4 \cdot 7\,H_2O$, forms deep-green crystals and is used as an electrolyte in nickel plating. *Cobalt oxide,* CoO, is used in making blue glass and blue decorations on chinaware. *Cobalt nitrate,* $Co(NO_3)_2 \cdot 6\,H_2O$, is a cherry-red deliquescent salt.

INKS

Composition. Inks were known as early as 2500 B.C. They were black and, like modern India ink, owed their color to carbon. There are many kinds of black ink; the composition of one form given by the United States government is as follows: tannic acid, 23.4 g; gallic acid, 7.7 g; ferrous sulfate, 30 g; dilute hydrochloric acid, 25 g; carbolic acid (phenol), 1 g; suitable blue dye, 3.5 g; sufficient water to make 1 liter.

Tannic acid and the closely related compound, gallic acid, are obtained from the bark of various trees and especially from nutgalls (abnormal growths produced on parts of trees that have been stung by certain insects). *Ferrous salts* do not form a color with tannic and gallic acids, but *ferric salts* produce a black tannate and gallate of iron. When the ink is used, the ferrous salt is oxidized by the air to a ferric salt, and this then forms the black iron compound. The dye called for in the formula is used to give a temporary color until the permanent color develops. The acid is necessary to keep the iron in solution. The carbolic acid acts as a preservative to keep the ink from molding.

Removal of ink and other stains from textiles. Some stains can be removed by simply washing the fabric with the appropriate solvent. Sirup stains, for example, can be removed by washing with hot water. Fruit stains and coffee stains can usually be washed out with boiling water. Carbon tetrachloride is a good solvent for oils and fats; turpentine dissolves fresh paint.

In some cases the stain can be removed only by the action of a reagent that will convert the stain substance into a soluble compound which can then be washed out with water. Thus a dilute solution of oxalic acid is effective in removing ordinary black ink stains, since the acid reduces the ferric salts in the ink to soluble ferrous salts which can then be washed out with water. In other cases the stain substance may be converted into colorless compounds by a mild bleaching agent, such as a dilute solution of sodium hypochlorite (the Javelle water of the druggist). In all such cases a test should first be made upon a small clipping of the textile to make sure that the substance used does not harm the textile. It is almost impossible to remove stains from silk because this textile is so sensitive to the action of solvents and reagents.

CHAPTER SUMMARY IN QUESTION FORM

1. Iron does not commonly occur free in nature; yet it has been familiar for more than four thousand years. Account for the fact that it has been known so long.

2. In what form does iron occur (*a*) in the earth's crust? (*b*) in the human body?

3. (*a*) Name three well-known forms of commercial iron. (*b*) What one element is present in all these forms in addition to the iron?

4. Answer the following in reference to the metallurgy of iron: (*a*) give the size and shape of the furnace in which the ores are reduced; (*b*) name four substances that enter the furnace, and state where each enters; (*c*) give the purpose served by each; (*d*) name three products that leave the furnace, and state where each leaves.

5. Name four elements whose removal from cast iron, wholly or in part, tends to improve the iron for commercial purposes.

6. Prepare a table that summarizes the facts about four of the chief varieties of iron under the following heads:

VARIETY	NAME OF FURNACE USED	MATERIALS ADDED TO FURNACE	PROPERTIES IN RELATION TO CARBON CONTENT, HARDNESS, ABILITY TO HOLD CUTTING EDGE OR TO BE WELDED, CAST, AND TEMPERED	USES

7. Name the elements that are used in various steel alloys.

8. What element or elements are added to iron to make it (*a*) very hard? (*b*) able to retain its cutting edge when hot? (*c*) able to resist acid corrosion? (*d*) stainless?

9. Prepare a table of information about five important compounds of iron under the following heads:

FORMULA	COMMON NAME	COLOR	PHYSICAL STATE	USES

10. How is it possible to have two series of iron salts, while aluminum forms but one?

11. Show by an equation written in the ionic form (*a*) how the ion Fe^{++} can lose an additional electron and become the ion Fe^{+++}; (*b*) how the ion Fe^{+++} can capture an electron and be changed to the ion Fe^{++}.

12. Explain why iron rusts more rapidly in *moist* air than in dry.

13. Give the composition of (*a*) nickel steel; (*b*) stellite; (*c*) nickel coin; (*d*) German silver; (*e*) stainless steel.

14. Explain how metal objects are electroplated with nickel.

15. Prepare a table of two columns in one of which are listed the various stains and in the other the method of removal.

THOUGHT QUESTIONS

1. (*a*) What is the difference between the basic open-hearth process and the Bessemer process? (*b*) Why is most of our steel today made by the open-hearth process rather than the Bessemer?

2. Suggest a reason why none of the metals so far studied occurs free in nature.

3. Give the common names of the ordinary hydrates of the sulfates of the following metals: (*a*) sodium, (*b*) magnesium, (*c*) iron (ferrous).

4. Contrast the relative advantages of iron and aluminum as materials for making cooking utensils.

5. Suppose you had a supply of pure iron and wished to prepare from it the compounds named. Write the equations showing the reactions you would use in the preparation of each: (*a*) ferrous sulfate; (*b*) ferric chloride; (*c*) ferrous sulfide; (*d*) ferric hydroxide.

6. Is there any relation between nickel-plated objects and galvanized iron?

OPTIONAL EXERCISES

1. Collect such objects as a nail, a bolt, a piece of watch spring, a needle, a knife blade, the base of a ring stand, a permanent magnet, an electromagnet, a chisel. Label each appropriately as cast iron, wrought iron, soft steel, or hard steel, and display them to the class.

2. Which of the ores of iron listed on page 574 contains the greatest percentage of iron?

3. What weight of iron would be required to make 500 lb of copperas?

CHAPTER XLIX

Copper, Mercury, and Silver; Photography

[Three Heavy Industrial Metals]

Name of Element	Atomic Number	Density	Melting Point	Electrons in Orbits
Copper (Cu) .	29	8.92	1083°	2 : 8 : 18 : 1
Silver (Ag) . .	47	10.5	960°	2 : 8 : 18 : 18 : 1
Mercury (Hg) .	80	13.546	– 38.9°	2 : 8 : 18 : 32 : 18 : 2

These three metals were among the six earliest known to man. To some extent they are found as free metals in nature, but their chief ores are sulfides. So their metallurgy is different from that of the metals so far studied (except zinc). All three metals are below hydrogen in the electromotive series; so water and dilute acids do not act on them unless air is present to help in their oxidation.

COPPER, THE GREAT ELECTRICAL METAL

Copper is an old acquaintance. Most of us can think of uses for copper for many of which no other metal will do as well. Copper wire is a necessity for many electrical purposes: for winding the armatures of all electrical motors and dynamos; for long-distance telephones (Fig. 436), power lines, and cable lines; for high-tension coils for the radio, and the starting and ignition systems of automobiles; for wiring our homes for light. Many of our most useful alloys contain large percentages of this metal.

What copper is like. Copper was the first metal to be used in any large way, because men found it native in metallic masses which were easily hammered into more useful tools than those made of stone. Its ruddy color and its shining polish gave it value for ornamental and ceremonial uses by the sun-worshipers.

Copper is a little heavier than iron, but melts at a lower temperature (1083°). It is fairly soft and very malleable, easily bent, and ductile; yet it is tough and strong. When perfectly pure it is second only to silver as a conductor of heat and electricity, but its conductance is much lessened by even a few tenths of 1 per cent of certain impurities.

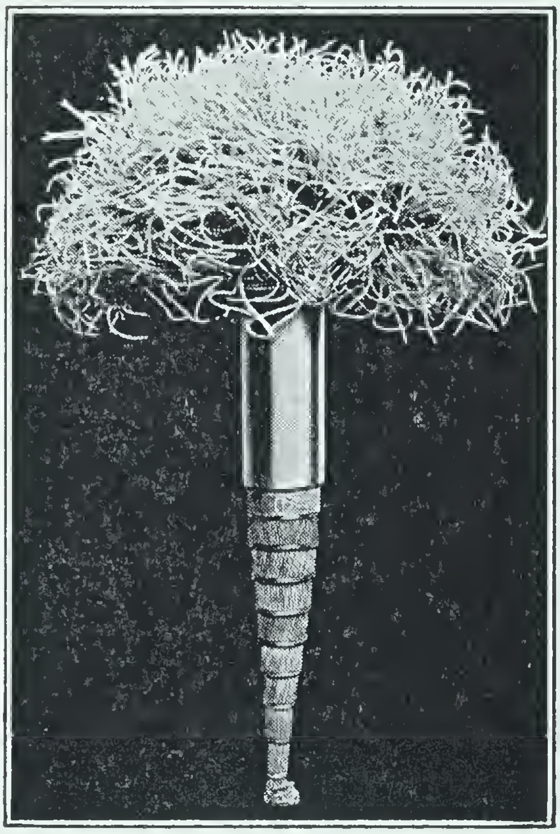


Fig. 436. Fine copper wire

A cable of 1200 pairs of wire frayed out at one end

Copper is found in many places. Copper is found native in northern Michigan, where the Indians mined it. Its mineral ores are most abundant in Arizona, Montana, Utah, and Michigan. The most valuable ores are these:

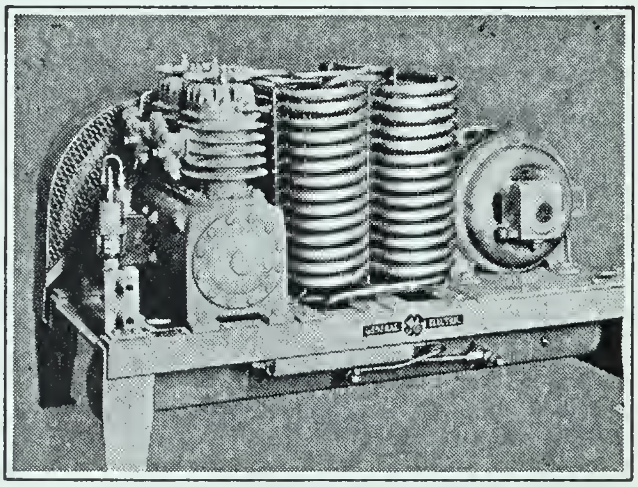
Chalcopyrite . . .	$CuFeS_2$
Chalcocite	Cu_2S
Bornite	Cu_3FeS_3
Malachite	$CuCO_3 \cdot Cu(OH)_2$

Metallurgy of copper. Ores in which copper is in the form of oxide or carbonate are often treated with dilute acid or ammonia, which changes the copper into a soluble salt. It is then recovered by electrolysis.

The metallurgy of the sulfide ores is too complicated to be described here. In its final stages the copper is present in a Bessemer converter (p. 577) as a liquid mixture of oxide and sulfide. The air is then shut off, and the following reaction takes place:

$$Cu_2S + 2\ Cu_2O \longrightarrow 6\ Cu + SO_2\uparrow$$

Copper got in this way is called *blister copper*, and contains about 3 per cent of impurities, including some gold and silver.



General Electric Company

Fig. 437. Some of the many uses of copper and its alloys in a household refrigerator

The refining of copper. The blister copper from the converter is cast into heavy anode plates. These are hung in a tank containing a solution of copper sulfate (together with

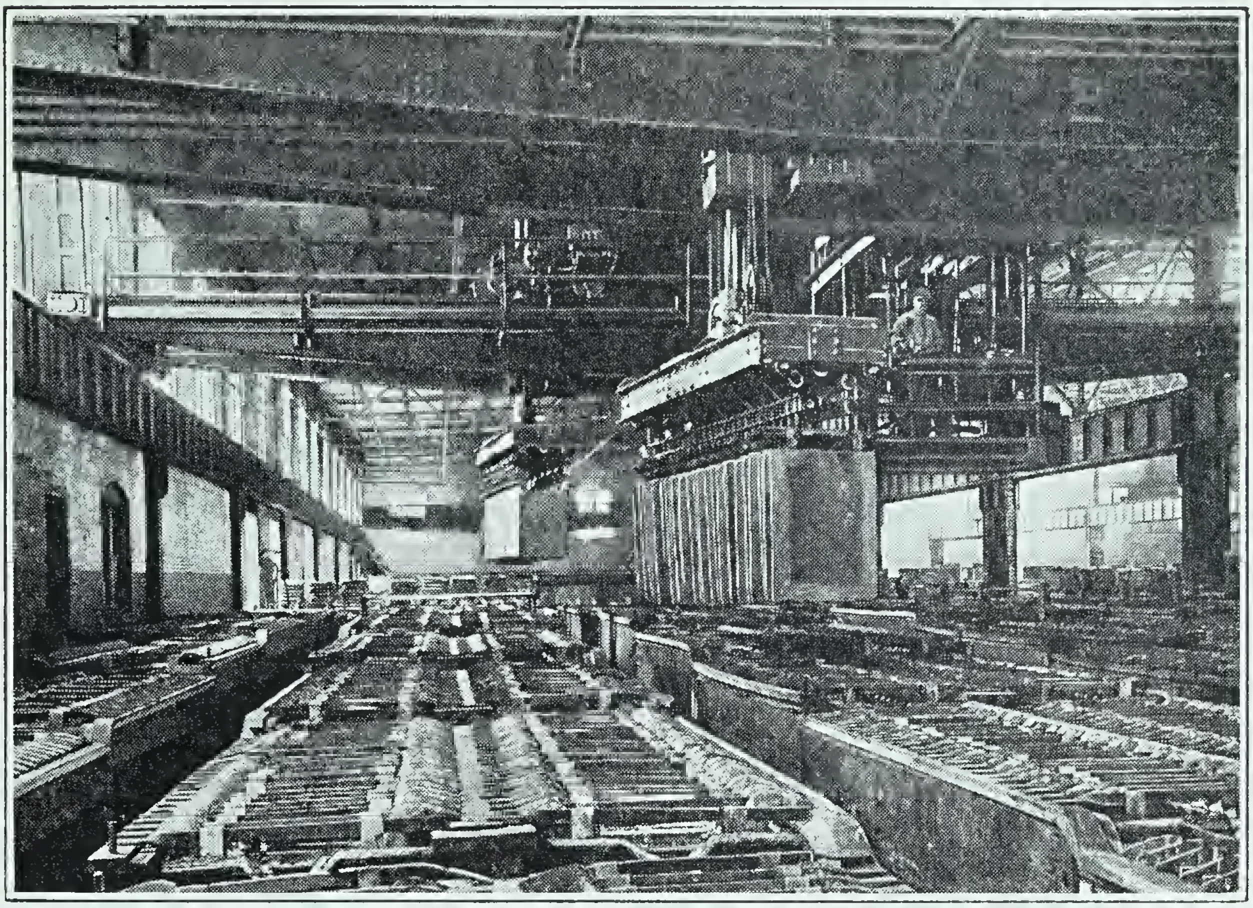


FIG. 438. Refining copper by electrolysis

The figure shows the pure copper cathode raised from an electrolytic cell so that the copper can be removed and the process repeated

some sulfuric acid). Facing each anode is hung a cathode made of thin sheet copper (Fig. 438). An electric current passing through such a cell dissolves copper from the anode and deposits it in pure form on the cathode. The impurities, including gold and silver, collect on the bottom of the cell.

How copper acts. Copper is below hydrogen in the electromotive series; so hydrochloric acid and dilute sulfuric acid have almost no action on it. Nitric acid or hot concentrated sulfuric acid first oxidizes it and then dissolves it (pp. 299 and 365). In moist air it slowly becomes covered with a film of bright-red oxide, Cu_2O, which soon changes into a green carbonate similar to the mineral malachite. Heated in the air the metal is easily oxidized to the black oxide, CuO.

Copper alloys. A very great variety of copper alloys are made, many of them having special trade names. A few of the most widely used are given in the table on page 592. In some cases other metals may be present, and the percentages are somewhat variable except in coin alloys.

Some Copper Alloys

Simple brasses, Cu, Zn
Leaded brasses, Cu, Zn, Pb
Tin brasses, Cu, Zn, Sn
Leaded brasses, Cu, Zn, Sn, Pb
Manganese brasses, Cu, Zn, Mn
German silver, Cu, Ni, Zn
Ordinary bronze, Cu, Sn
Phosphor bronze, Cu, Sn, P
Zinc bronze, Cu, Sn, Zn
Lead bronze, Cu, Pb, Sn
18-carat gold, Au, 75%; Cu, Ag
14-carat gold, Au, 58%; Cu, Ag
Gold coin, Au, 90%; Cu, 10%
Silver coin, Ag, 90%; Cu, 10%
Nickel coin, Cu, 75%; Ni, 25%
Sterling silver, Ag, 92.5%; Cu, 7.5%

Some idea of the great weight of such alloys used is got from the fact that the liner *Queen Mary* has over three million pounds of copper and its alloys in her structure and fittings, each of her four propellers having a weight of thirty-five tons of manganese bronze. Mechanical refrigerators are said to use a million pounds of copper each week in their manufacture (Fig. 437).

Electrotyping. Books are often printed from electrotype plates, which are made as follows: The page is first set up in type. Powdered graphite is dusted over a plate of wax, and the face of the type is pressed into this wax by a strong press. The graphite prevents the wax from sticking to the type. The pressure packs the graphite into an electrically continuous sheet, coating the impression of the type in the wax. This graphite-coated wax is now made the cathode in an electrolytic cell containing a copper salt in solution. The copper is deposited as a thin sheet upon the letters in wax. When this is pulled off the wax, it is a perfect copy of the type.

Two series of copper compounds. Copper, like iron, forms *two series* of compounds. In the *cuprous* compounds, it is univalent; in the *cupric* compounds it is bivalent. Cuprous compounds have few uses. The oxide, Cu_2O, is a bright-red solid and is sometimes used to give a ruby color to glass. Cuprous sulfide, Cu_2S, and cuprous chloride, $CuCl$, are other examples of cuprous salts.

Cupric compounds. Cupric salts are easily made by dissolving cupric oxide in acids or, when insoluble, by precipitation. When crystallized most of them are blue or green. Since they are so much more familiar than the cuprous salts, they are often called merely copper salts.

***Cupric oxide* (CuO).** This is a black solid obtained by heating copper in excess of air. In the laboratory it is used as an oxidizing agent; in refining oil it is used for removing sulfur from the crude oil.

***Cupric sulfate* ($CuSO_4$).** When crystallized from water, copper sulfate forms large, blue crystals of the hydrate $CuSO_4 \cdot 5\,H_2O$, called *blue vitriol* or *bluestone.* The salt is a by-product in silver refining and is also made by the oxidation of pyrite containing copper sulfide:

$$CuS + 2\,O_2 \longrightarrow CuSO_4$$

Blue vitriol is used in electrotyping, in copper refining, and in the manufacture of insecticides. Like all copper salts it is poisonous, especially to lower forms of life. When it is added even in minute quantities to water containing green pond scum (algae), these plants are quickly killed.

***Cupric sulfide* (CuS).** Cupric sulfide (CuS) is easily prepared as a black, insoluble precipitate by the action of hydrogen sulfide upon a solution of a copper salt:

$$CuSO_4 + H_2S \longrightarrow CuS \downarrow + H_2SO_4$$

Tests for cupric ions (Cu^{++}). A bright piece of iron (such as a nail) becomes coated with copper when dipped in a solution of a copper salt:

$$Cu^{++}, SO_4^{--} + Fe \longrightarrow Fe^{++}, SO_4^{--} + Cu$$

Ammonia added to a solution of a copper salt produces a deep blue color.

MERCURY, THE ONE LIQUID METAL

Mercury — a strange metal. The alchemists were greatly interested in mercury because it is a heavy, silvery metal like silver but is a *liquid at ordinary temperatures*. They thought that if they could only harden it, it would be real silver. So it was called *quicksilver*, or "live silver."

Its chief ore is the sulfide (HgS), called *cinnabar*, which has a beautiful red color. It was mined in early Roman times, to be used as a paint pigment. We can make this same compound by heating mercury and sulfur together; so made, it has a better color than the mineral and is called *vermilion.* Mercury is heavier than iron or copper, having a density of 13.546. It boils at 365° and freezes at – 38.9°.

How we get mercury, and how it acts. It is very easy to get mercury from cinnabar. When the ore is roasted in the air, the sulfur burns, and the mercury is set free as a vapor. The vapor is then condensed as in ordinary distillation. California, Texas, Spain, and Italy are producers of mercury.

Toward acids mercury acts very much like copper. Just below its boiling point it combines slowly with oxygen to form mercuric oxide, HgO. At a little higher temperature this oxide decomposes into mercury and oxygen. These reactions led to the discovery of oxygen (p. 79).

Uses of mercury. We use mercury in a number of scientific instruments, such as the thermometer and the barometer. Gases that are soluble in water we collect over mercury. In some large plants mercury is used instead of water in the boilers that run the engines. With many other metals mercury forms alloys that are called *amalgams*, most of which are solids. Some of these are used in dentistry, and in one process gold is dissolved from its ores by mercury. An important use is in the mercury-vapor lamp.

The mercury-vapor lamp. When cold, mercury vapor does not conduct the electric current. In a vacuum tube containing some *heated* vapor an arc is easily started, and a peculiar light fills the tube. This light is rich in green and ultraviolet rays. Such a tube is called a Cooper-Hewitt lamp. This lamp is much used to light factories, as a photographic light, and to provide ultraviolet light for medical purposes.

If one electrode within such a tube is iron and the other mercury, the vapor will conduct the current in one direction only. By this means an alternating current becomes a direct current, and the lamp is called a *rectifier*.

Fluorescent lamps. It has recently been discovered that the mercury-vapor lamps are greatly improved in the quality of the light emitted and that they operate at less cost when the inside surface of the tubes is coated with

Westinghouse Electric and Manufacturing Co.

FIG. 439. A store lighted with fluorescent lamps

thin layers of certain compounds. These compounds, principally the silicates and tungstates of some of the metals, are known as *phosphors.*

The tubes are first evacuated and a drop of mercury added to each tube. A small amount of argon (under low pressure) is also added to facilitate starting. When the current is connected, the argon conducts the current, and the resulting heat vaporizes the mercury, which then becomes a conductor. The ultraviolet light emitted by the hot vapor causes the phosphors to fluoresce — hence the name of the lamp. These lamps have come into wide use and promise much for the future in lighting, especially for large rooms and buildings (Fig. 439).

Compounds of mercury. Like copper, mercury forms two series of salts, in which it has a valence of 1 or of 2. The *mercuric* compounds are the more important.

Mercurous chloride (HgCl) is insoluble and is precipitated as a white solid by adding sodium chloride to a solution of mercurous nitrate:

$$HgNO_3 + NaCl \longrightarrow HgCl\downarrow + NaNO_3$$

In medicine it is called *calomel.* Mercuric oxide (HgO) is usually made by heating mercuric nitrate:

$$2\ Hg(NO_3)_2 \longrightarrow 2\ HgO + 4\ NO_2\uparrow + O_2\uparrow$$

Mercuric chloride, $HgCl_2$, is made by heating a mixture of common salt and mercuric sulfate:

$$2\ NaCl + HgSO_4 \longrightarrow HgCl_2\uparrow + Na_2SO_4$$

The mercuric chloride vaporizes from the heated mixture and is condensed in cool vessels. It is called *corrosive sublimate* and is very poisonous. It is used in surgery as an antiseptic.

SILVER, THE METAL THAT GIVES US PHOTOGRAPHY AND MOVIE REELS

Silver has a long history. Silver has been known and prized from the earliest times. The Romans were very fond of it and called it *argentum.* They got it, along with lead, from mines in Spain and used it for coins and ornaments. The alchemists put it next to gold (the sun metal) in purity and value, and indicated it by a crescent, the symbol for the moon.

Where silver is found. Silver is nearly always found as the sulfide, Ag_2S, along with the sulfides of other elements, especially copper, lead, and arsenic. So its metallurgy is carried on along with that of other metals, chiefly lead. Mexico and the United States are the great silver countries; our center for silver is the northern Rocky Mountain states.

Metallurgy of silver. Many plans for silver metallurgy are in use because of the many kinds of ore. In this country the mixed sulfides of silver and lead are reduced together to a silver-lead alloy. A very ingenious method (the *Parkes* process) is then used to get the silver away from the lead.

The alloy is melted together with about 2 per cent of zinc. The melted zinc is very slightly soluble in the liquid alloy, and floats on it like oil on water (p. 506). At this temperature silver is about three thousand times more soluble in liquid zinc than in liquid lead. So, if the liquid is well stirred, the silver nearly all leaves the lead and dissolves in the zinc, the silver-zinc alloy rising to the top when stirring is stopped. This layer is then skimmed off and distilled. The zinc passes off as vapor, which is condensed and used over again. The silver is left behind, and is purified by electrolysis.

FIG. 440. Silver ingots

A portion of a week's supply at the Eastman Kodak factory

Silver itself. Silver is a heavy, soft, white metal and very ductile. It is the best of all metals as a conductor of electricity. It melts at 963° (a little lower than copper) and alloys easily with many other metals.

It is not oxidized by either water or air; but sulfur and its compounds tarnish it, forming black silver sulfide, Ag_2S. Concentrated sulfuric acid acts on it as it does on copper. Even dilute nitric acid oxidizes it and forms the very soluble silver nitrate, $AgNO_3$.

How we use silver. *Silver coins* are alloys of 90 per cent silver and 10 per cent copper, while *sterling silver* is 91.6 per cent silver and 8.4 per cent copper. Tableware is either sterling silver or an alloy of some kind heavily plated with silver. In many Oriental countries both pure silver and sterling silver are widely used for ornaments of all kinds. *Mirrors* and *silvered glassware* are made by covering the surface of the glass with a solution of a silver salt and adding a reducing agent. The reduced silver deposits as a shining film on the surface of the glass. Apart from coinage and silverware, the great need that silver supplies and that no other metal meets is in *photography* (Fig. 440).

Compounds of silver. Silver is univalent in all its compounds; so their formulas are like the formulas of mercurous and cuprous salts. Silver nitrate (lunar caustic) ($AgNO_3$) has been described (p. 300).

The halogen salts of silver. The chloride, the bromide, and the iodide of silver (the silver halides) are insoluble in water and in acids. So they are precipitated by adding a soluble halogen salt to a solution of silver nitrate:

$$Ag^+, NO_3^- + K^+, Cl^- \longrightarrow Ag^+Cl^- \downarrow + K^+, NO_3^-$$

These compounds are rapidly decomposed by sunlight (or ultraviolet light), especially if they are mixed with organic matter, such as gelatin. It is upon this fact that the art of photography depends.

PHOTOGRAPHY

The chemistry of photography. To understand the chemistry of photography, let us set about making a photograph step by step (Fig. 441).

Making the sensitive plate or film. The plate or film must be very sensitive to the very short waves in sunlight which are beyond the violet waves in the visible spectrum and which for this reason are called ultraviolet light. The manufacturer makes a colloidal dispersion of silver bromide in gelatin, and spreads it as a thin film on a glass plate or a cellulose nitrate or acetate film. This sensitive plate is then dried and is ready for use. The whole preparation must be carried on in red light only.

Making the exposure. The sensitive plate is put in a camera, and the image of the object to be photographed is focused on the plate. When exposure is made, the silver salt is partially reduced by the light, and the extent of the reduction at each point on the plate is proportional to the intensity of the light falling on it. The result is an image on the plate which is not visible and is called *latent.* It is made visible by *developing* the plate. The development of the plate and the making of the print are described in connection with Figs. 442, 443.

Toning the print. To give the photograph a softer appearance and an attractive color, it may be *toned.* The print in black silver is dipped into a solution of gold or platinum salts. These metals are below silver in the electromotive series; so the silver passes into solution and is replaced by the other metals. Gold makes a reddish-brown print, while platinum gives it a steel-gray tone.

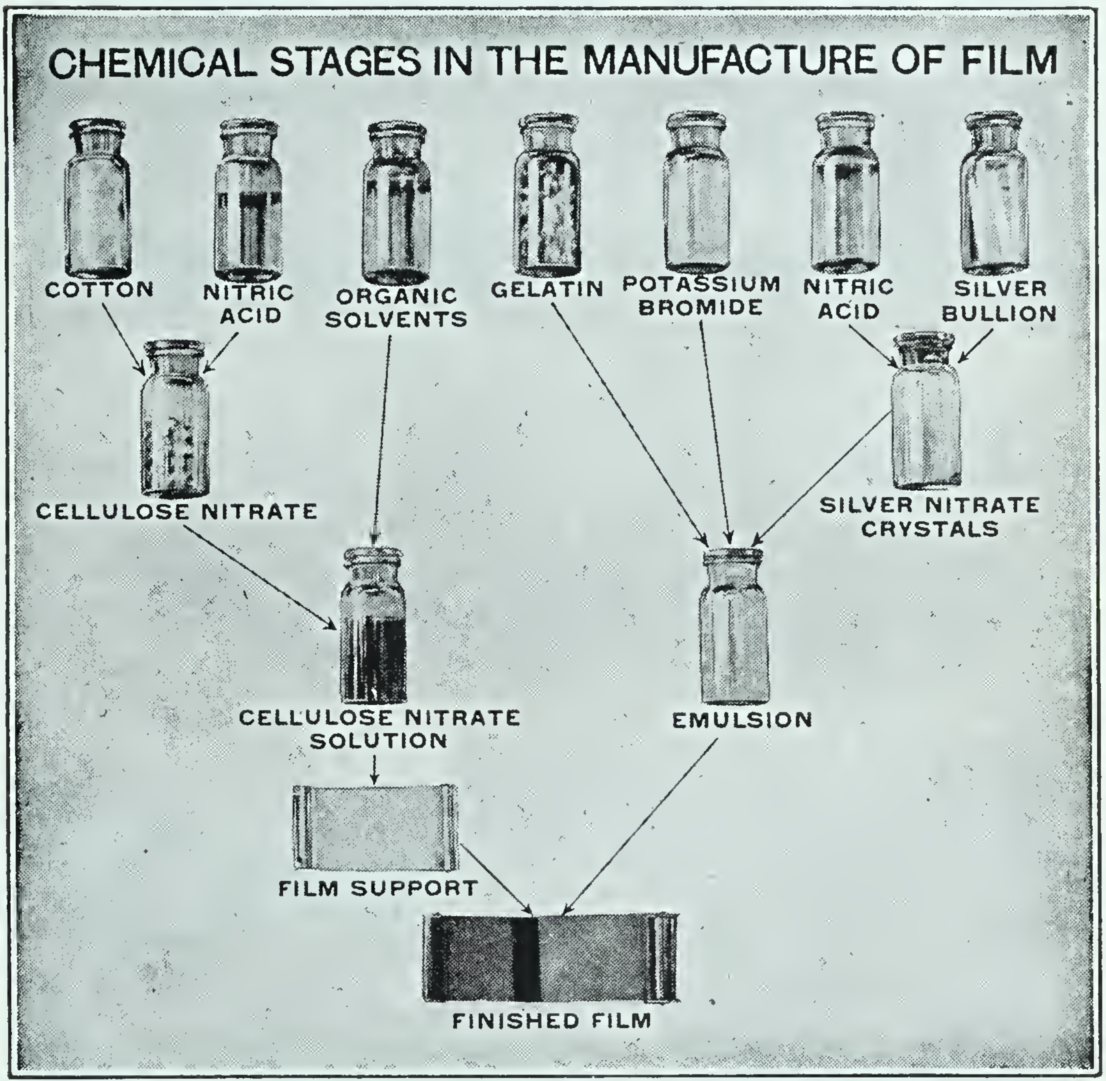

CHEMICAL STAGES IN THE MANUFACTURE OF FILM
COTTON
NITRIC ACID
ORGANIC SOLVENTS
GELATIN
POTASSIUM BROMIDE
NITRIC ACID
SILVER BULLION
CELLULOSE NITRATE
SILVER NITRATE CRYSTALS
CELLULOSE NITRATE SOLUTION
EMULSION
FILM SUPPORT
FINISHED FILM

FIG. 441. Steps in the production of the photographic film

The various raw materials used in the production of the film are shown in the upper row. The cotton (cellulose) and nitric acid react to form cellulose nitrate, which is dissolved in a mixture of alcohol and ether to form the cellulose nitrate solution. The silver and nitric acid react to form silver nitrate. This is then mixed with gelatin and potassium bromide. The silver nitrate and potassium bromide react to form silver bromide, which is dispersed in the gelatin in the form of an emulsion. The emulsion is then spread over the film support and dried, thus forming the finished film. (Courtesy of the Eastman Kodak Co.)

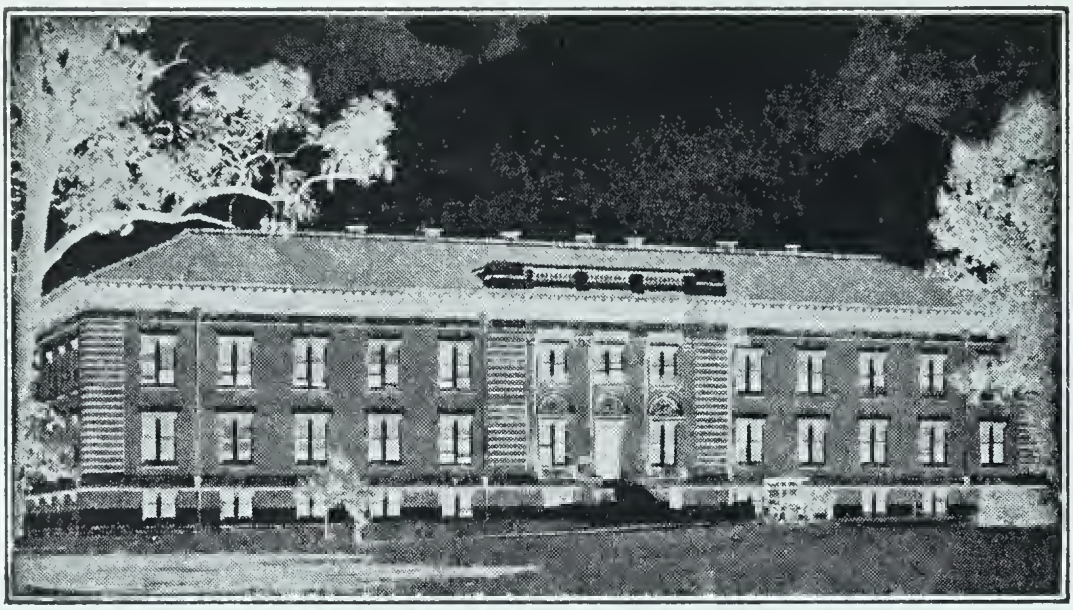


Fig. 442. The negative plate

The photographic plate or film, after exposure in the camera, is immersed in a solution of a reducing agent (the developer) which reduces the silver salt that has been acted upon by the light to black metallic silver. The unaffected silver salt is then dissolved with sodium thiosulfate ("hypo"), leaving a picture of the object photographed on the plate, but with the lights and horizontal directions exactly reversed. A plate so prepared is called a *negative*

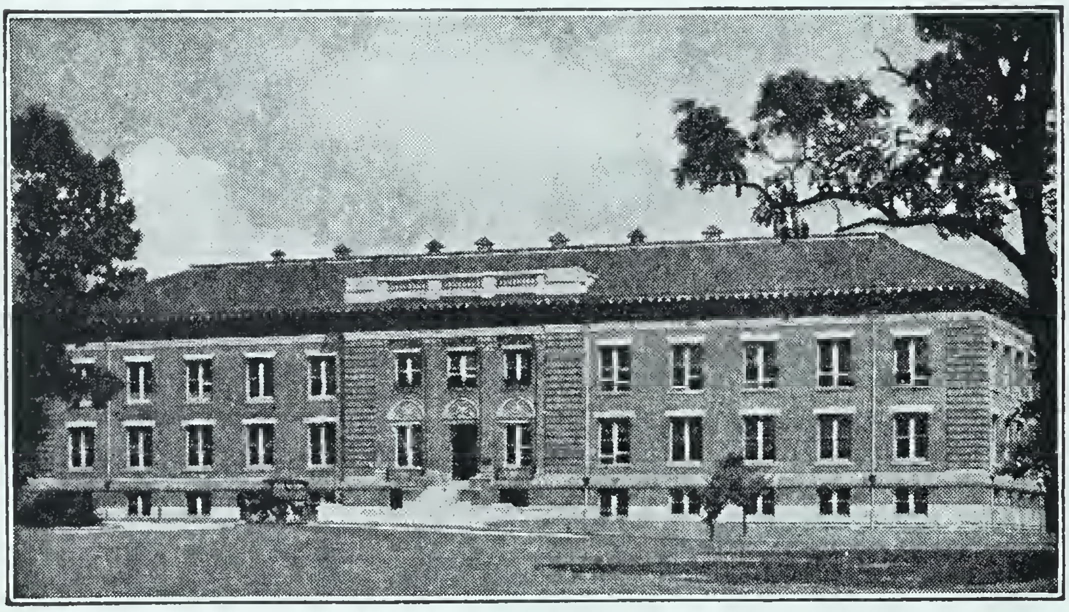


Fig. 443. The positive print

The print is made from the negative. The photographic paper on which the print is to be made is placed under the negative and exposed to the light. The paper is then treated with a developer, and the unaffected silver salts are dissolved off with "hypo," as in the preparation of the negative. Since the darkest places on the negative cut off the most light, the lights of the print will be the reverse of those of the negative; in other words, they will correspond to those of the object photographed

CHAPTER SUMMARY IN QUESTION FORM

1. Name three uses of copper, each of which is dependent upon a different property.

2. Mention five properties of copper that make it a useful metal.

3. What states furnish most of our copper?

4. Give the names and composition of two important copper ores.

5. Show by a diagram how impure copper is refined.

6. "Copper, like iron, forms two series of compounds." (*a*) How do we distinguish between the two series? (*b*) What is the valence of copper in each? (*c*) Give the name and formula of a compound belonging to each series.

7. Write the equation for the preparation, and state one important use, of (*a*) black copper oxide; (*b*) blue vitriol.

8. In what respect does mercury differ from all other metals?

9. State the properties of mercury that adapt it (*a*) for use in barometers and thermometers; (*b*) for the manufacture of amalgams; (*c*) for changing an alternating electric current into a direct current.

10. A mercury thermometer could be used for obtaining the temperatures between what limits?

11. Make a table that deals with four important compounds of mercury under the following heads:

FORMULA	COMMON NAME	PHYSICAL STATE	COLOR	ONE USE

12. State the properties of silver that make it a useful metal.

13. Give the names, formulas, and physical appearance of three important compounds of silver.

14. Illustrate by diagram the method of electroplating with silver.

15. Distinguish between (*a*) pure silver, (*b*) sterling silver, and (*c*) silver-plated articles.

16. (*a*) Give the steps in the preparation of silver chloride from a bar of pure silver. (*b*) Write the equation for the last step in the process, and tell why the reaction goes to completion.

17. Why is silver bromide used in photography?

18. (*a*) What chemical change does silver bromide undergo in the preparation of a negative? (*b*) Why is the negative so called?

19. Why does the sensitiveness of both the photographic plate (or film) and the print cease after they are dipped into a solution of "hypo"?

20. Study the electromotive series (p. 261) and explain why gold salts are used in *toning* prints, rather than the cheaper copper and tin salts.

THOUGHT QUESTIONS

1. Why should we expect the metals studied in this chapter not to be acted upon by water, nor by acids with the liberation of hydrogen?

2. In electroplating with silver, why use silver in place of some cheaper metal or of carbon as an anode?

3. Write the equations for the reactions (if any) that occur when copper is treated with each of the following acids: (*a*) hydrochloric; (*b*) nitric; (*c*) dilute sulfuric; (*d*) concentrated sulfuric.

4. Give two reasons for adding copper to the silver used in silver coins.

5. What is the distinction (*a*) between blue vitriol and green vitriol? (*b*) between copper sulfate and copperas?

6. The alchemists believed that a piece of iron immersed in a solution of blue vitriol is changed into copper. What reason had they for this belief?

7. What undesirable property has nitrocellulose as a material for making photographic films?

8. How could you distinguish (*a*) the oxide of copper, (*b*) the oxide of mercury, (*c*) the oxide of zinc, each from the others?

9. Suppose you were given the following substances: sulfuric acid; hydrochloric acid; nitric acid; marble; copper; zinc. What gases could you prepare from these substances?

10. Suppose you allowed mercury to come in contact with a gold ring. What would be the result?

OPTIONAL EXERCISES

1. A silver dollar weighs approximately 26.5 g. What weight of (*a*) silver nitrate and of (*b*) copper nitrate could be prepared from such a coin?

2. Suppose you had a supply of silver and wished to prepare 100 g of silver bromide. (*a*) Write the equations for the reactions. (*b*) What weight of silver should you have to use?

CHAPTER L

Tin and Lead; Paints

[Two Metals That Look Alike but Are Very Different]

NAME OF ELEMENT	ATOMIC NUMBER	DENSITY	MELTING POINT	ELECTRONS IN ORBITS
Tin (Sn)	50	7.31	231.85°	2 : 8 : 18 : 18 : 4
Lead (Pb)	82	11.34	327.5°	2 : 8 : 18 : 32 : 18 : 4

A case of mistaken identity. Now and then we read about some prisoner who has served years of a sentence. Then it is discovered that he is not the guilty man but looked so much like the criminal that he was taken for him. The papers say it was a case of "mistaken identity."

The Romans made that kind of mistake about tin. They had long used lead for many practical purposes, and tin looked so much like it that they thought it was merely a kind of lead. They called it "white lead" to distinguish it from common lead, which they called "black lead."

TIN, THE PROTECTOR OF IRON

How the ancients got their tin. In the palmy days of Egypt and Chaldea the dwellers in a very small country called Phoenicia were the sea-roving merchants of the Mediterranean. More than 1000 years B.C. they knew about the heavy tinstone of what is now Cornwall, and carried the tin from that source to be sold throughout Asia Minor to *harden* copper; that is, to change it into bronze alloy.

We have little tin. Tin is the one important metal which, so far as we know, nature has failed to give abundantly to the United States, and our production of the metal is very small — merely a few tons annually. The world's supply comes largely from the Malay States (Fig. 444), the Dutch East Indies (Bangka), Siam, and Bolivia. Tin is found chiefly as an impure oxide, SnO_2, called *tinstone* or *cassiterite.*

Tin is a typical metal. Pure tin, called *block* tin, is a soft, white metal with a silverlike appearance and luster. It melts

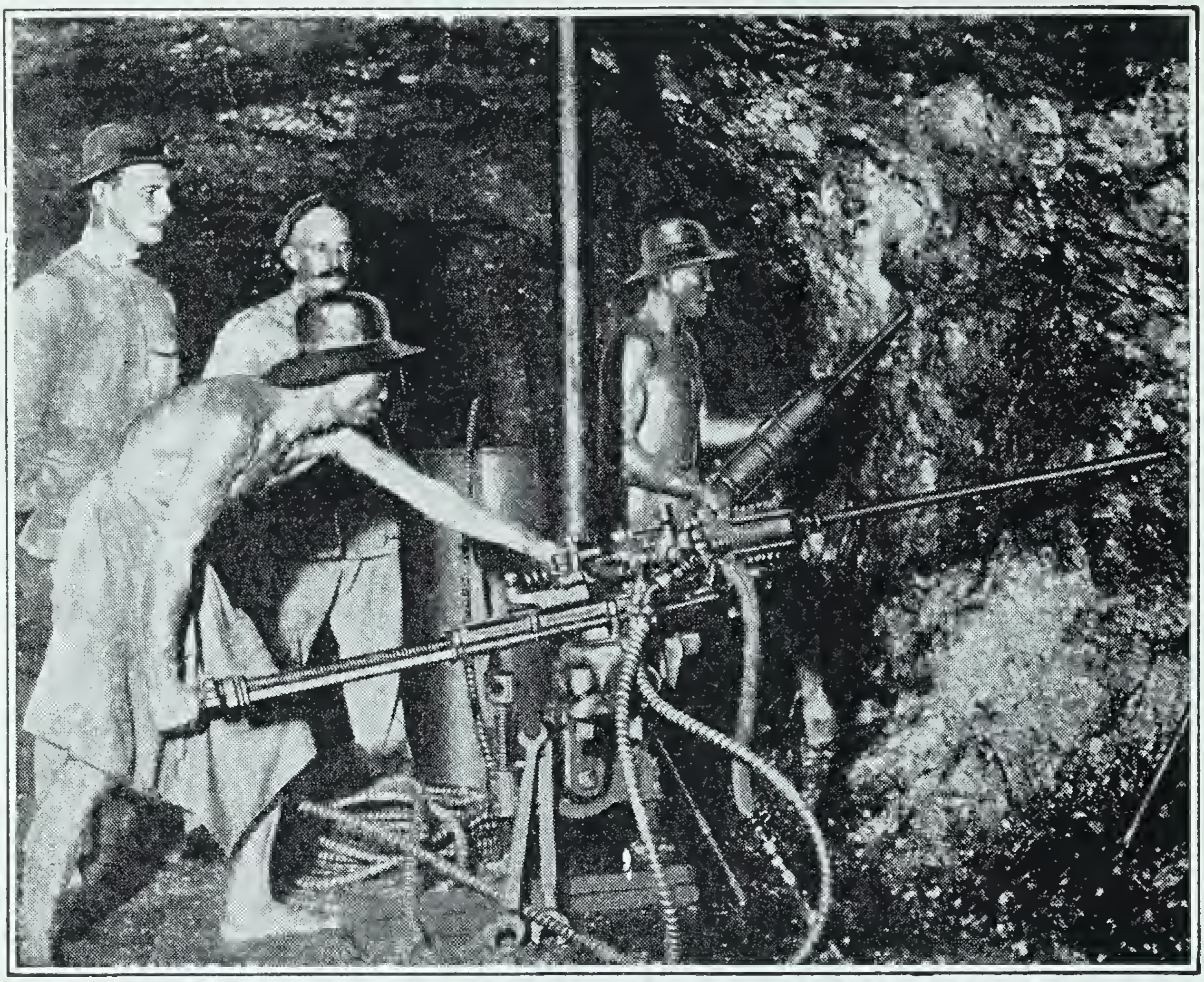


FIG. 444. Mining in the Malay States

readily (at 231.85°) and is somewhat lighter than copper. **It is malleable and can be rolled out into very thin sheets, forming** *tin foil.* Most tin foil, however, contains a considerable percentage of lead, and aluminum foil is now used more than tin foil. When kept at a low temperature for a long time, tin slowly changes into a gray powder. This change to an allotropic form, called tin disease (Fig. 445), sometimes destroys tin objects in very cold countries.

Metallurgy. Since tin ore is an oxide, the metallurgy of tin is easily understood. The chief difficulty is to free the ores from troublesome impurities before reducing the oxide. Then the purified ore is heated with coal in a simple reverberatory furnace:

$$SnO_2 + C \longrightarrow Sn + CO_2\uparrow$$

Tin is not an active metal. Under ordinary conditions **tin is unchanged by air or moisture; but at a high temperature it burns, forming the oxide** SnO_2. Dilute acids have **little**

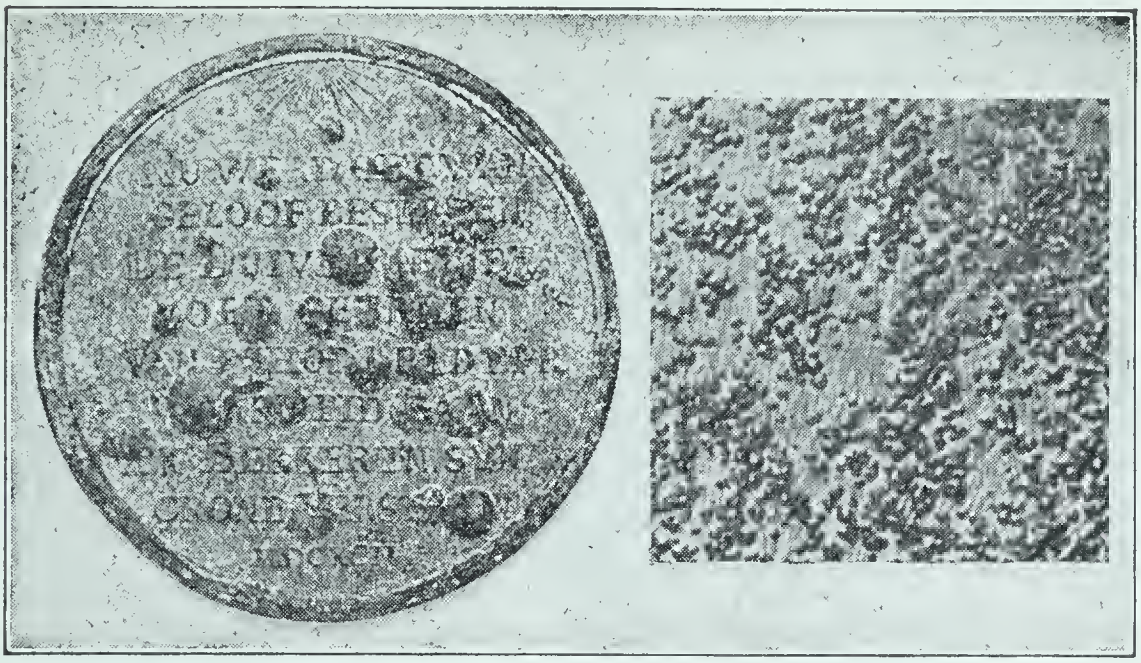


FIG. 445. Tin objects that have been kept at a low temperature for a long time, showing the partial change into the gray powdered form (tin disease)

effect upon it, although concentrated acids attack it readily. Concentrated hydrochloric acid slowly changes it into the chloride $SnCl_2$.

Uses of tin. The United States uses up about half the world's annual output of tin. By far the largest quantity of tin is used in the making of *tin plate.* This is done by dipping thin sheets of iron (or copper) into the melted tin, very much as iron is galvanized (Fig. 406). Small pipes of block tin are used instead of lead for conveying pure water or liquids containing dilute acids, such as soda water. Many useful alloys contain tin, including various bronzes and bearing metals. *Soft solder* is an alloy of tin and lead, usually in equal parts.

Soldering and brazing. To be of use in joining two metal surfaces, a solder must have several definite properties. (1) It must have a rather low melting point; (2) when melted it must wet the surfaces of the clean metals, so as to flow evenly over them; (3) when it has cooled, it must make a strong joint.

To get clean surfaces free from oxide a suitable *flux* must be used. This will either *dissolve* the oxide as fast as it forms or float it away from the metal surface, or *reduce* it again to metal. The usual fluxes are zinc chloride, ammonium chloride, tin chloride, or material containing one of these. Rosin is sometimes used.

Compounds of tin. Tin forms two series of metallic compounds. In the *stannous*, the tin is bivalent, as is illustrated in the compounds SnO, SnS, $SnCl_2$. In the *stannic*, it is quadrivalent, as is shown in the formulas SnO_2, SnS_2, $SnCl_4$. Nearly all tin salts are white.

Chlorides of tin. *Stannous* chloride ($SnCl_2$) is made by dissolving tin in concentrated hydrochloric acid and evaporating the solution to crystallization. If metallic tin is heated in a current of dry chlorine, *anhydrous stannic* chloride ($SnCl_4$) is obtained as a heavy colorless liquid which fumes strongly in moist air. A great deal of tin in the form of stannic chloride is recovered from scrap tin plate by the action of chlorine. From solution in water a solid hydrate is obtained of the formula $SnCl_4 \cdot 5\ H_2O$.

The chlorides of tin are much used as mordants in dyeing processes, in calico-printing, and to give weight to silk.

Reducing action of stannous ions. Stannous ions (Sn^{++}) tend to lose two more electrons to become oxidized to stannic ions (Sn^{++++}). Therefore they are strong *reducing* agents:

$$Hg^{++}, Cl^{-}{}_2 + Sn^{++}, Cl^{-}{}_2 \longrightarrow Hg + Sn^{++++}, Cl^{-}{}_4$$

LEAD: A VERY OLD METAL WITH SOME INTERESTING PROPERTIES

What the ancients did with lead. Articles made of lead have been found in very old Egyptian ruins, and there is no doubt that it was used from early times. The Babylonians wrote on lead tablets. The Romans called it *plumbum* and used it for water pipes, as we do today. Before them the Cretans had used it for the same purpose. It has been man's water-carrier for a great many centuries.

What lead is like. Nearly everyone knows what lead looks like. It is a heavy metal which has a bright luster on a freshly cut surface but soon tarnishes on exposure to air. It is soft, melts easily, has little strength, and is a poor conductor.

We are a lead country. The United States produces nearly half of the world's supply of lead, the chief lead-producing states being Missouri, Utah, Idaho, and Oklahoma. The chief ore is *galenite* (PbS) (Fig. 446), and it usually contains some silver, as well as small percentages of other metals.

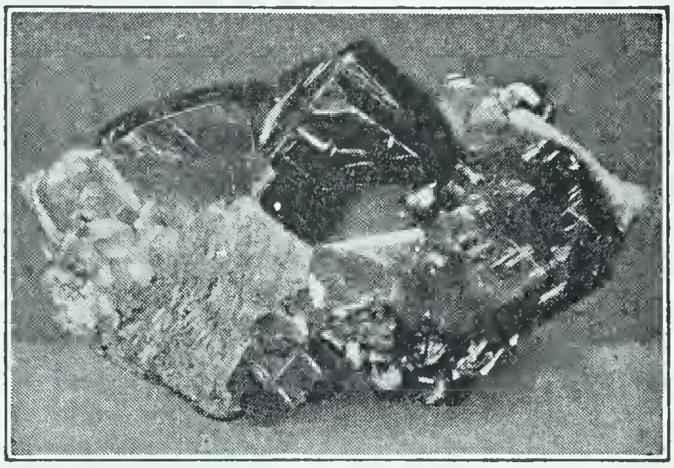


FIG. 446. A crystal of galenite embedded in calcite

Metallurgy. To get lead from its ores is a rather complicated process of roasting and reduction. As first got, the crude lead is alloyed with any silver or gold that was in the ores, and with varying small percentages of other metals. The impure lead is melted in an open furnace with free access of air. Iron and other easily oxidized impurities are oxidized and, as oxides, float on the heavier lead, from which they can be skimmed off as a scum. Silver and gold stay in the lead and are recovered from it either by the Parkes process (p. 596) or by electrolysis of the lead, as in the case of crude copper.

Some reactions of lead. When lead is heated in the air, it forms a yellow oxide (PbO). In the presence of dissolved oxygen most acids, even very weak ones, act on lead, forming soluble lead salts. Neither hydrochloric nor sulfuric acid, when cold or dilute, has much action on the metal, because their lead salts are insoluble and quickly make a protective covering on the lead. When hot and concentrated, both these acids attack it to a greater extent.

Lead a metal of many uses. Lead finds many important uses in the industries, chiefly in making storage batteries; in linings for sulfuric-acid plants; for covering cables of electric wires; in alloys of various kinds, such as shot, antifriction metals, type metal, solder, and pewter (lead and tin); and in water pipes for plumbing. *About one third of the annual production of lead is used in making paint* and is permanently lost.

Compounds of lead. In nearly all its compounds lead is bivalent, but in a few it has a valence of four. All ordinary salts of bivalent lead are white unless the acid radical has a marked color (for example, lead iodide is scarlet).

All lead compounds are more or less poisonous, and are *cumulative* in their effects. Even very small repeated doses accumulate in the system and finally cause lead poisoning. All lead workers — those who work with paints, batteries, sheet lead, and the like — must watch for symptoms of such trouble.

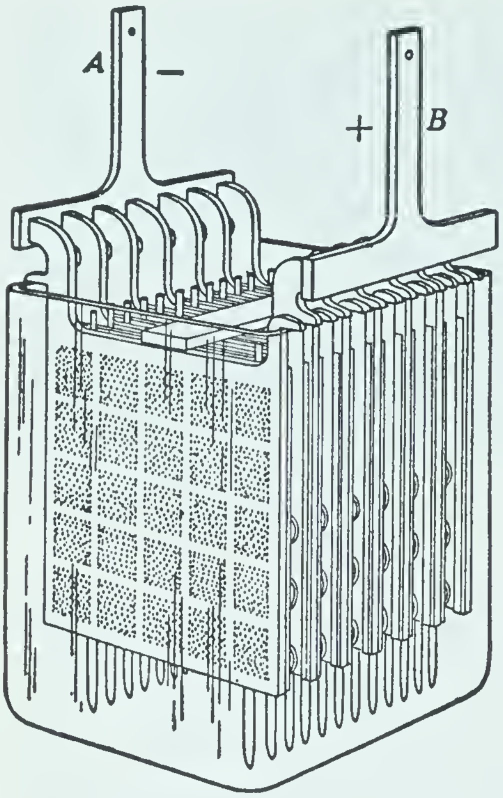


FIG. 447. A seven-plate storage battery

Lead sulfide (PbS). In nature this compound is found as the well-crystallized mineral *galenite* (Fig. 446). The crystals have much the same color and luster as pure lead. In the laboratory lead sulfide is made as a black precipitate, by the action of hydrogen sulfide on a soluble lead salt:

$$Pb(NO_3)_2 + H_2S \longrightarrow PbS\downarrow + 2\ HNO_3$$

Lead oxides. Lead forms a number of oxides, the most important of which are the following:

1. ***Litharge (PbO).*** This oxide can be made by oxidizing lead at about 600°, but is largely supplied as a by-product in silver-refining. In color it ranges from yellow and light brown to orange, according to the way it has been made. Its chief use is in making glazes and flint glass.

2. ***Red lead, or minium (Pb_3O_4).*** Minium is made by heating lead (or litharge) to about 450° in a current of air. It is a heavy powder of a beautiful red color and is much used as a pigment for painting structural iron, since it protects the metal from rusting. Plumbers use it, mixed with linseed oil, to make gas-tight joints in pipes.

3. ***Lead peroxide (PbO_2).*** The peroxide can be made as a chocolate-brown powder by oxidizing litharge under proper conditions. It is the active material on the positive plates of the usual type of storage battery.

Storage batteries. In a storage battery (Fig. 447) the negative plates are lead, usually alloyed with a little antimony. The positive plates are layers of lead peroxide on a lead support. The electrolyte is dilute sulfuric acid. When current is being drawn from the battery, the lead cathode plates are being oxidized (lead ions being formed). The electrons set free from the lead atoms pass through the external wires to the anode, constituting an electric current in the wire. The lead-peroxide anode plates are being reduced (tetravalent lead becoming divalent lead). On both plates Pb^{++} ions are therefore being formed. These give insoluble lead sulfate with the SO_4^{--} ions of the electrolyte, which sticks to the two plates. The equation is

$$Pb + PbO_2 + 2\ H_2SO_4 \rightleftarrows 2\ PbSO_4 + 2\ H_2O$$

Sulfuric acid is in this way withdrawn from the electrolyte, decreasing its density. When the battery is being charged, all these changes are reversed, bringing the battery to its original state. A test of the density of the electrolyte shows how far the battery has been discharged and when it needs charging.

Composition of white lead. The normal carbonate of lead ($PbCO_3$) is found to some extent in nature and can be made in the laboratory; but a *basic* carbonate can be made much more easily. This is a compound of lead carbonate and lead hydroxide, $(PbCO_3)_2 \cdot Pb(OH)_2$, called *white lead.* It is made on a very large scale as a white pigment and as a body for paints which are to be colored with other pigments.

Manufacture of white lead. White lead is often made by electrolytic methods, but the old *Dutch process* is still largely employed. It has been used for centuries, although with a good many improvements (Fig. 448).

Other important compounds of lead. Some other important compounds of lead are as follows:

Lead nitrate ($Pb(NO_3)_2$)	white soluble crystals
Lead chloride ($PbCl_2$)	white needles, soluble in hot water, slightly soluble in cold water
Lead sulfate ($PbSO_4$)	an insoluble white crystalline powder
Lead acetate ($Pb(C_2H_3O_2)_2 \cdot 3\ H_2O$)	a soluble white salt called *sugar of lead*
Lead chromate ($PbCrO_4$)	used as a pigment in paint (*chrome yellow*)
Lead arsenate ($Pb_3(AsO_4)_2$)	used as an insecticide

Paints. A paint consists of two essential parts: the vehicle and the pigment.

1. ***The vehicle, or liquid medium.*** The vehicle consists of several components: (1) A *drying oil,* such as linseed oil, obtained from flaxseed, which will take up oxygen and dry to a hornlike substance. (2) A *thinner,* of turpentine or of suitable distillates from petroleum, to reduce the viscosity sufficiently for easy working. The thinner evaporates after the paint has been applied. (3) A *drier*; this is a catalyst to promote the oxidation (drying) of the oil. The driers are made by boiling various inorganic compounds with the drying oil. The compounds commonly used are oxides, hydroxides, or salts of manganese, lead, or cobalt.

2. ***The pigment.*** The pigment, or solid part of the paint, consists of finely divided compounds suspended in the vehicle. The pigment provides the necessary durability as well as the desired color. It must have good hiding power, or opacity. The pigment may be (1) a white solid, such as white lead, sublimed white lead (a basic lead sulfate), zinc oxide, lithopone (p. 545), titanium oxide, or a mixture of titanium oxide with barium sulfate, calcium sulfate, or any other white pigment. Or the pigment may be (2) a color compound such as iron oxide, lead chromate, burnt clays of various kinds, ultramarine, lampblack, Prussian blue, and many others. Sometimes color pigments are made by coagulating a colloidal compound in the presence of an organic dye. The dye is adsorbed by the precipitate, forming a pigment called a *lake.*

Varnishes. Until recent years the *solid* portion of a varnish was made of natural gums or resins from trees, together with *rosin.* This is a resinlike body got from pine trees along with turpentine (Fig. 451). At present the solids are mostly artificial, gumlike materials made from a large variety of organic compounds.

In the usual kind of varnish the *liquid medium* is *tung oil.* This is a drying oil pressed from the nuts of the tung tree, a native of China and now cultivated in some of our Southern states. The resin, together with a drier, is dissolved in the oil by heating the mixture (Fig. 449). The boiled product is

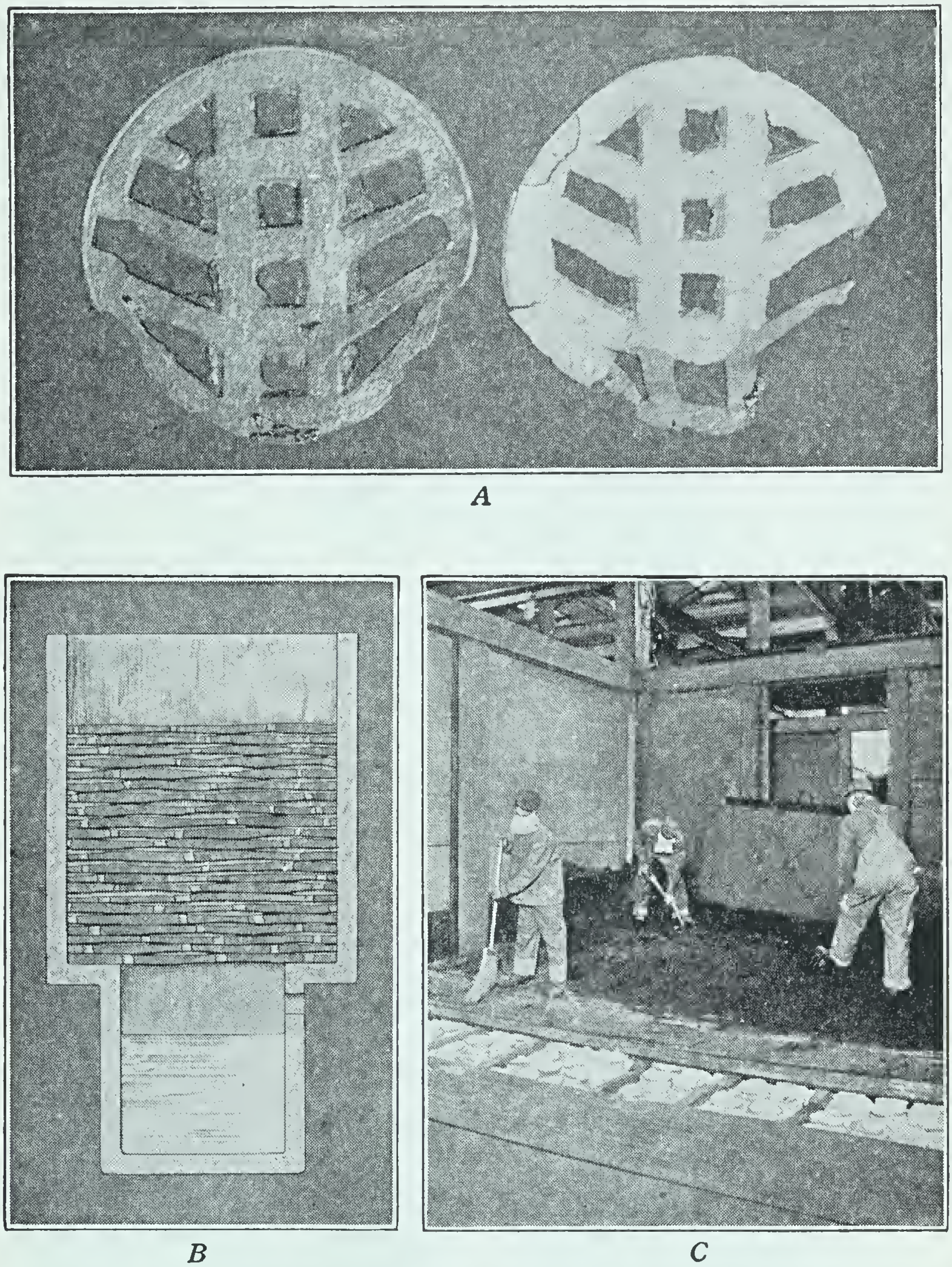


FIG. 448. Steps in making white lead by the Dutch process

A: Lead plates (buckles) before and after exposure to acetic acid and carbon dioxide. *B:* The lead plates placed in a crock, the lower part of which is filled with acetic acid. *C:* The crocks filled with the lead plates and acetic acid are placed in tiers and covered with spent tanbark (the bark of a tree rich in tannin, such as oak bark). The tanbark slowly ferments, setting free carbon dioxide. Enough heat is given off in this process to vaporize the acetic acid. The acetic acid and the carbon dioxide together convert the lead into white lead. The figure shows the workmen removing the tanbark after the action is complete. The lead plates, now converted into white lead, are seen where the covering has been removed

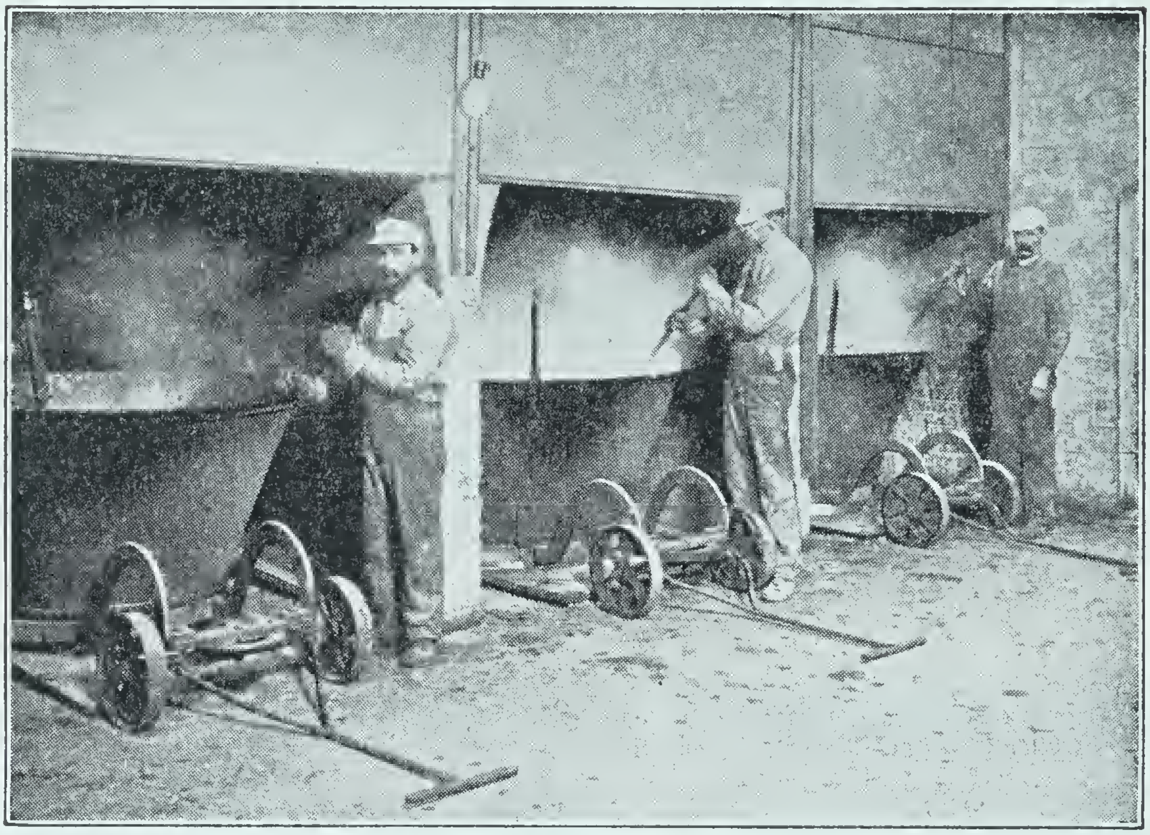


Fig. 449. Making varnish

The resin is placed in large iron kettles set on wheels, and melted over a fire. The kettles are then withdrawn, and the resin is dissolved in linseed oil or tung oil, together with oil of turpentine or a similar liquid, such as benzine

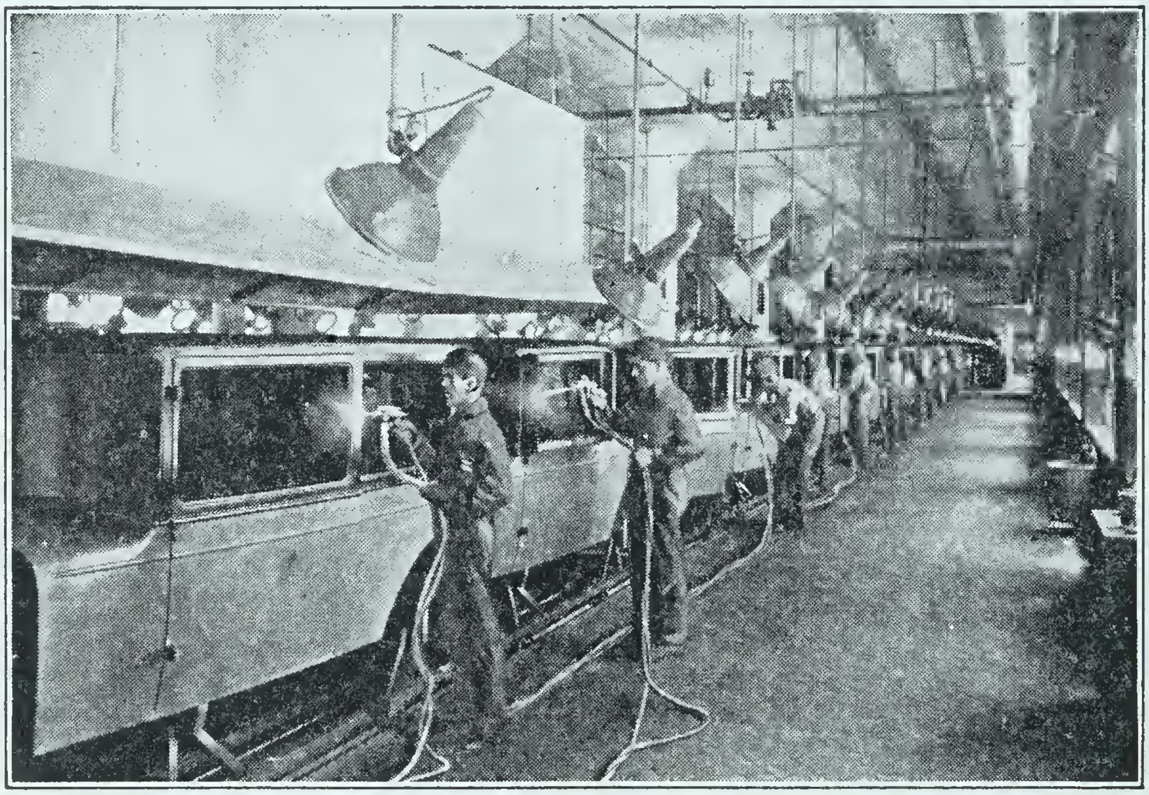


Fig. 450. Spraying automobile bodies with lacquers

then thinned with turpentine or with a similar volatile solvent, such as benzine. When the varnish is painted on a surface, the thinner evaporates, and the oil oxidizes (as with paints) and dries, along with the resin.

A second kind of varnish is called *spirit* varnish. In this the resin is dissolved in a volatile solvent (turpentine or alcohol). When a spirit varnish is painted on a surface, the solvent evaporates, leaving a film of the resin.

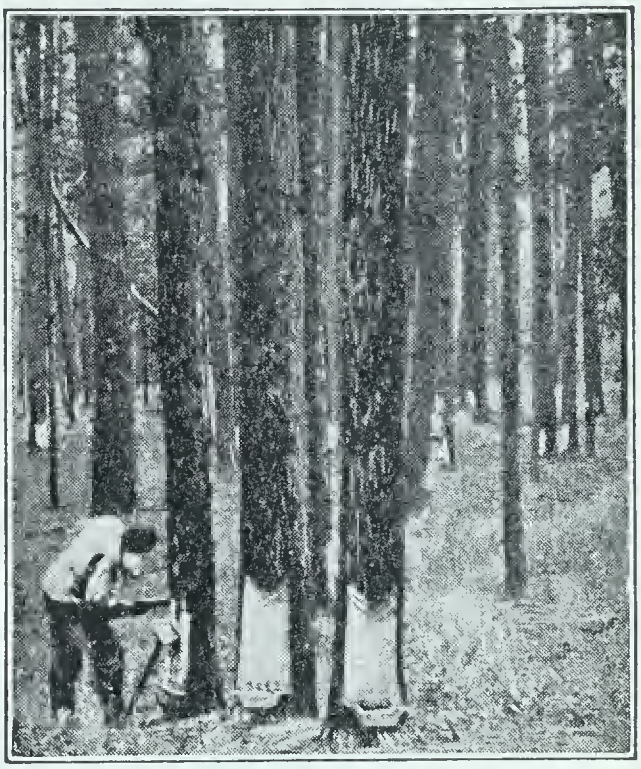


Fig. 451. Making incisions in pine trees

From these incisions exudes a resinous mass, the raw material from which ordinary rosin and spirits of turpentine are prepared

Lacquers. A lacquer is a special kind of varnish containing cellulose derivatives. Lacquers have been made for many years, but their properties have been greatly improved in recent times, owing to the development of synthetic resins and to the discovery of new cotton-cellulose derivatives that are much more soluble than those formerly used.

The modern lacquer is composed of (1) specially soluble ("half-second") cellulose nitrate or acetate (p. 464); (2) a resin, including any of the synthetic varnish resins and some others (this gives hardness and luster to the finished surface); (3) a *plasticizer*, to prevent cracking on drying (castor oil or other organic compounds); (4) a solvent, usually some of the modern synthetic solvents; (5) a diluent, usually a coal-tar hydrocarbon such as toluene or a similar petroleum distillate; (6) a pigment color.

Lacquers dry very rapidly and are best applied with a spray gun. By their use an automobile can be sent from the paint shop in two days or less, instead of the two weeks formerly required (Fig. 450). One can have a damaged fender relacquered and can drive off in an hour. These lacquers resist weather well.

CHAPTER SUMMARY IN QUESTION FORM

1. (*a*) Give the name and composition of the chief ore of tin, and (*b*) state how the tin is separated from the ore.

2. What are the properties of tin that make it a useful metal?

3. (*a*) What is tin plate? (*b*) To what other product is it similar?

4. (*a*) What two properties of solder make it possible to join two metal surfaces by its use? (*b*) How does a flux aid in the operation?

5. Tin forms two series of compounds. (*a*) What is the valence of tin in each? (*b*) How do we distinguish between the two in name? (*c*) Illustrate by giving the names and formulas of the two chlorides.

6. What evidence have we that lead has long been known?

7. Give (*a*) the name, (*b*) the formula, and (*c*) the uses of each of the oxides of lead.

8. State the chemical changes taking place when a storage battery is delivering a current.

9. Give the chemical name, the common name, and the composition of a lead compound that is prepared on a large scale for use in making paints.

10. (*a*) Name the two essential ingredients of paint, and (*b*) state the purpose served by each.

11. Name two properties of lacquers that make them useful in the automobile industry.

THOUGHT QUESTIONS

1. Mention three products each of which is protected by a coating of pure metal.

2. What salts other than those of tin are used as mordants?

3. How is the condition of a storage battery tested? Explain.

4. The air in a chemical laboratory is likely to contain hydrogen sulfide from time to time. Which of the following pigments would be best adapted for painting the walls of such a laboratory: lithopone, zinc oxide, or white lead?

5. What substances obtained from trees are used in the paint industry?

6. What properties in common have benzine, spirits of turpentine, alcohol, and benzene that adapt them for use in the paint industry?

7. Linseed oil is more expensive than cottonseed oil. Why not use the latter in making paint?

8. After the name of each compound in column *A* write the number of the formula in column *B* that represents the composition of the compound:

A	*B*
caustic soda ----	(1) Fe_3O_4
zinc white ----	(2) $CuSO_4 \cdot 5\,H_2O$
hydrated lime ----	(3) $Na_2SO_4 \cdot 10\,H_2O$
Glauber's salt ----	(4) $HgCl$
sal soda ----	(5) $AgNO_3$
copperas ----	(6) Pb_3O_4
white lead ----	(7) $(CaSO_4)_2 \cdot H_2O$
plaster of Paris ----	(8) $HgCl_2$
Epsom salt ----	(9) $Ca(OH)_2$
saltpeter ----	(10) $MgSO_4 \cdot 7\,H_2O$
blue vitriol ----	(11) KNO_3
calomel ----	(12) ZnO
baking soda ----	(13) $Na_2CO_3 \cdot 10\,H_2O$
magnetite ----	(14) $NaOH$
corrosive sublimate ----	(15) $NaHCO_3$
red lead ----	(16) $(PbCO_3)_2 \cdot Pb(OH)_2$
lunar caustic ----	(17) $FeSO_4 \cdot 7\,H_2O$

OPTIONAL EXERCISES

1. Calculate the percentage of lead (*a*) in each of the oxides of lead; (*b*) in white lead.

2. Collect a set of samples of various materials that contain lead or tin, label them, and exhibit them to the class.

CHAPTER LI

Manganese and Chromium

[Both the Elements and Their Compounds Are Important]

MANGANESE, THE METAL THAT MAKES ALL GOOD STEEL POSSIBLE

Manganese ores. The important ore of manganese is *pyrolusite*, MnO_2. It was while working with a sample of this mineral that Scheele showed it contains a metal different from iron. By treating it with hydrochloric acid he discovered chlorine.

In commercial quantities pyrolusite is found chiefly in the Soviet Union, India, and Brazil, but smaller or less concentrated deposits of manganese minerals are found in many countries. In very small quantities manganese compounds are present in all fertile soils.

Manganese itself. Pure manganese is rarely prepared, because it has no special uses. It is much like iron in many of its properties, but is harder to reduce from its ores, melts at a lower temperature (1260°), and is crystalline and brittle.

Ferromanganese. When pyrolusite, iron oxide (hematite), and carbon are heated together in an electric furnace, the two oxides are reduced and form an iron-manganese alloy. If this is rich in manganese, it is called *ferromanganese.*

This alloy is of the greatest importance in the steel industry, and about fifteen pounds of manganese (in this form) is added to the liquid iron for every ton of steel made. The manganese does two things: it combines with any sulfur or oxygen in the liquid iron and carries them into the slag, and if enough is added, part remains in the steel and makes a valuable manganese-alloy steel that is very hard. Manganin (Cu, 84 per cent; Mn, 12 per cent; Ni, 4 per cent) is used in electrical instruments as resistance wire. Manganese bronze (Mn and Cu of various composition) resists corrosion and is used for propeller blades on ships.

Compounds of manganese. Up to this point in our study we have thought of a metal as always a base-forming element

(p. 500). But there are a number of elements that are metals in all their physical properties and that have *three or four different valences.* In low valences (2 or 3) their hydroxides are *bases*; but when these are strongly oxidized, they give oxides of higher valences (6 or 7) that are *anhydrides of acids.*

Manganese is a metal of this kind. In the presence of a *reducing agent* the manganese of a compound is reduced to a valence of 2 (sometimes 3) and forms the cation of a salt, Mn^{++}. An *oxidizing* agent oxidizes manganese to a valence of 7 (sometimes 6), corresponding to an oxide Mn_2O_7, which is the anhydride of the acid $HMnO_4$. In this compound the manganese plays the part of an acid-forming element, giving the anion MnO_4^-.

Manganese salts. Like iron, manganese can act as either a bivalent or a trivalent metal. The manganous salts, in which the metal is bivalent, are the common ones. In both formulas and chemical properties these are similar to ferrous salts. They are pink in color and are nearly all hydrated. For example, we have the sulfate, $MnSO_4 \cdot 4\,H_2O$, and the chloride, $MnCl_2 \cdot 4\,H_2O$.

Potassium permanganate ($KMnO_4$). Potassium permanganate is a salt of the unstable permanganic acid ($HMnO_4$). It is made by heating pyrolusite with potassium hydroxide and an oxidizing agent, dissolving the product in water, and neutralizing the excess alkali with an acid. It is the easiest permanganate to get, and forms deep-purple soluble crystals.

Potassium permanganate is an oxidizing agent. A solution of potassium permanganate is a powerful oxidizing agent, especially if sulfuric acid is also present. Under these conditions both the potassium and the manganese are changed into sulfates (positive ions), and oxygen is given up for oxidizing action, as shown in the equation

$$2\,K^+, MnO_4^- + 3\,H^+{}_2, SO_4^{--} \\ \longrightarrow K^+{}_2, SO_4^{--} + 2\,Mn^{++}, SO_4^{--} + 3\,H_2O + 5\,[O]$$

The two MnO_4^- ions are *reduced* to two Mn^{++} ions, and six H^+ ions are oxidized.

Both sodium and potassium permanganates are valuable oxidizing agents and are used as disinfectants.

CHROMIUM, THE METAL THAT BRIGHTENS OUR MOTORCARS

Most of us think of chromium as a silvery plating on the trimmings of our motorcars and household plumbing fixtures. The metallurgist thinks of it as an alloy metal that makes steel hard and stainless.

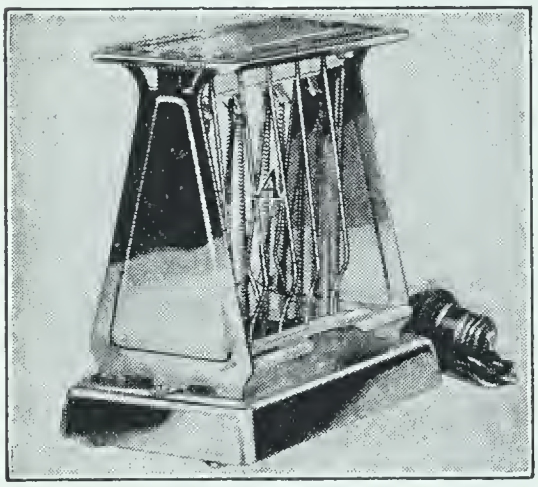


Fig. 452. Electric toaster

Resistance wire (*A*) of nichrome is used in electric toasters and similar heating appliances

Ferrochromium. Except as a plating on other metals, chromium is rarely prepared as a pure metal. Its only important ore is called *chromite* and has the formula $Fe(CrO)_2$. This is found in many countries, but the largest commercial supply comes from Africa (Rhodesia). When this ore is reduced with carbon in an electric furnace, a rich alloy of iron and chromium results, called *ferrochromium.*

To make chromium steel of a given composition, the necessary weight of ferrochromium is added to the liquid steel just before it is poured. Stainless steels (Fig. 453) all contain chromium; some grades contain nickel also; all are resistant to rust. *Nichrome* is an alloy of nickel and chromium much used for resistance wire in electrical heaters (Fig. 452).

Compounds of chromium. Like manganese, in lower valences chromium acts as a base-forming metal, having the trivalent ion Cr^{+++}. This gives a series of chromic compounds which are green or violet in color. Among these are the oxide, Cr_2O_3, used as a green pigment; and chrome alum, $KCr(SO_4)_2 \cdot 12\,H_2O$, used as a mordant and in the rapid tanning of leather.

High-valence compounds of chromium. In the higher valence of 6, chromium together with oxygen forms the anion of several important acids.

Chromates. The chromates are salts of *chromic acid,* H_2CrO_4. This formula resembles the one for sulfuric acid; but chromic acid is much less stable than sulfuric acid and

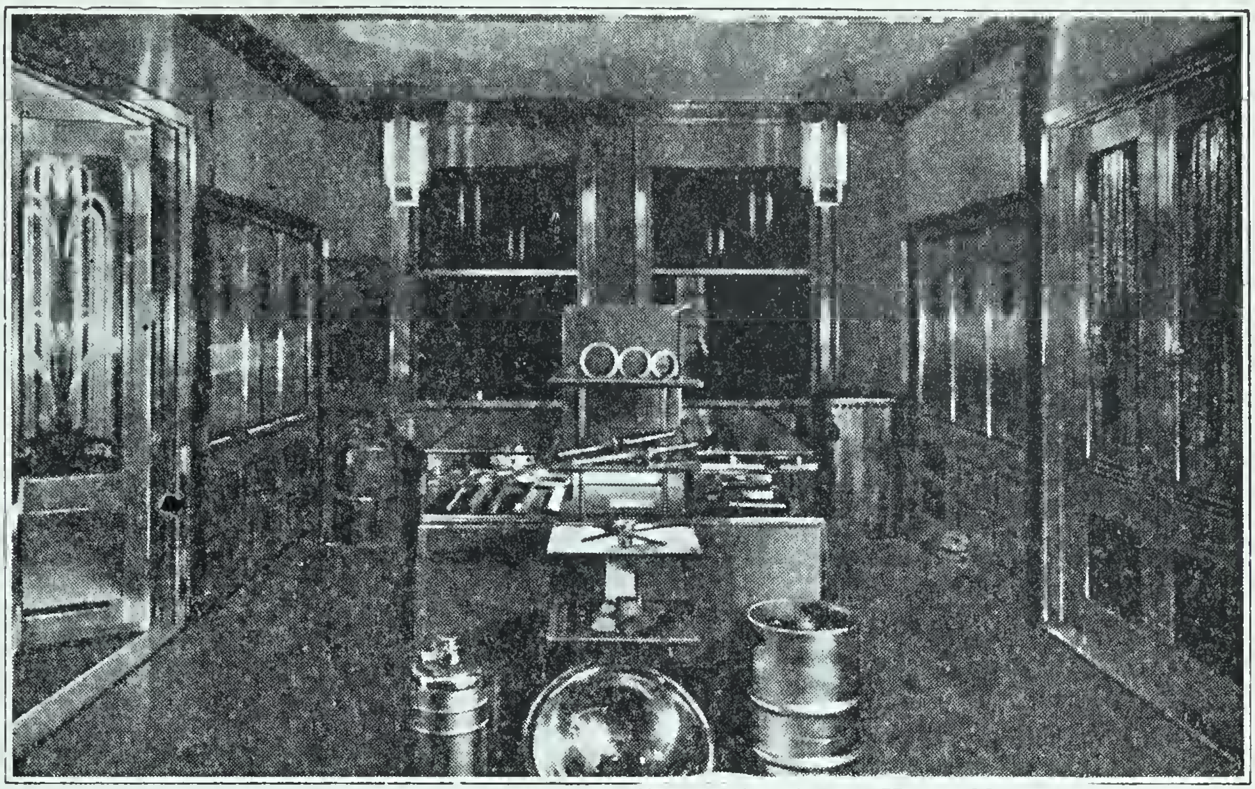


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FIG. 453. The walls of the room, as well as the articles in it, are made of stainless steel

is a much stronger oxidizing agent. Its solutions are red in color, and its salts, the chromates, are red or yellow. The alkali chromates are soluble, but nearly all other chromates are insoluble and can be made by precipitation:

$$Pb(NO_3)_2 + K_2CrO_4 \longrightarrow PbCrO_4\downarrow + 2\ KNO_3$$

Lead chromate (*chrome yellow*) and barium chromate are used as yellow pigments of different shades.

Potassium dichromate ($K_2Cr_2O_7$). When potassium chromate (K_2CrO_4) is treated with the right amount of sulfuric acid, the potassium salt of *dichromic acid* ($H_2Cr_2O_7$) results:

$$2\ K_2CrO_4 + H_2SO_4 \longrightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$$

This is the best-known dichromate and the most familiar chromium compound. It crystallizes in large, brilliant-red crystals. Potassium dichromate, as well as the corresponding sodium salt ($Na_2Cr_2O_7$), is used in many industries as an oxidizing agent, especially in making organic compounds. Proteids treated with a dichromate become resistant to water when exposed to light; this is the foundation of the photoengraving industry, in which $(NH_4)_2Cr_2O_7$ is commonly used.

When either chromates or dichromates act as an oxidizing agent, the chromium is reduced to the Cr^{+++} ion.

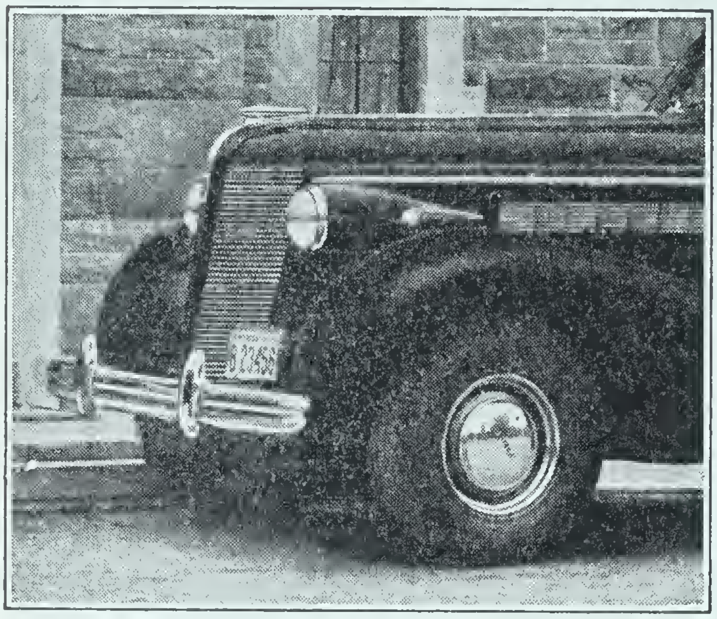


FIG. 454. Chromium plating

The headlights, radiators, bumpers, and wheels of automobiles are often chromium plated

Chromium electroplating. Chromium has come into very wide use for electroplating automobile parts (Fig. 454), plumbing fixtures, office furniture, and many other metal objects. It can be plated on most metal surfaces; but the best results are got by plating first with copper, then with nickel, and finally with chromium. The chromium plating then makes a brilliant surface that is harder than steel and is not tarnished or corroded by weather or by dilute reagents. The electrolyte is usually a solution of chromic acid (H_2CrO_4) together with some sulfate ions.

CHAPTER SUMMARY IN QUESTION FORM

1. Name two elements in the laboratory preparation of which manganese dioxide is used.

2. What is the chief use of manganese?

3. Name three alloys that contain manganese.

4. (*a*) Which of the metals sometimes form acids? (*b*) Give an example of the formula of such an acid.

5. One of the most useful of the compounds of manganese is potassium permanganate. (*a*) Describe its appearance. (*b*) What property makes it a useful compound? (*c*) Is the manganese in this compound an acid-forming or a base-forming element?

6. What important alloy of chromium is used in electrical heaters?

7. Mention two important uses of chromium.

8. Potassium dichromate is the principal compound of chromium. (*a*) Compare its appearance with that of potassium permanganate. (*b*) Is it an oxidizing or a reducing agent?

THOUGHT QUESTIONS

1. For what purpose is manganese dioxide used in the glass industry?

2. Manganese dioxide in powdered form closely resembles powdered charcoal. How could you easily distinguish between the two?

3. When manganese dioxide is used in the preparation of chlorine, what compound of manganese is formed?

4. What important sulfates have we studied that are (*a*) colorless? (*b*) colored?

5. When sulfurous acid (colorless) is added to a solution of potassium permanganate (colored), a colorless solution results. Explain.

6. The common cleaning fluid used in the laboratory for cleaning test tubes and beakers consists of a mixture of sodium dichromate and sulfuric acid. Why is it so efficient?

CHAPTER LII

A Variety of Elements

[Some Very Rare, Others Abundant; All Useful]

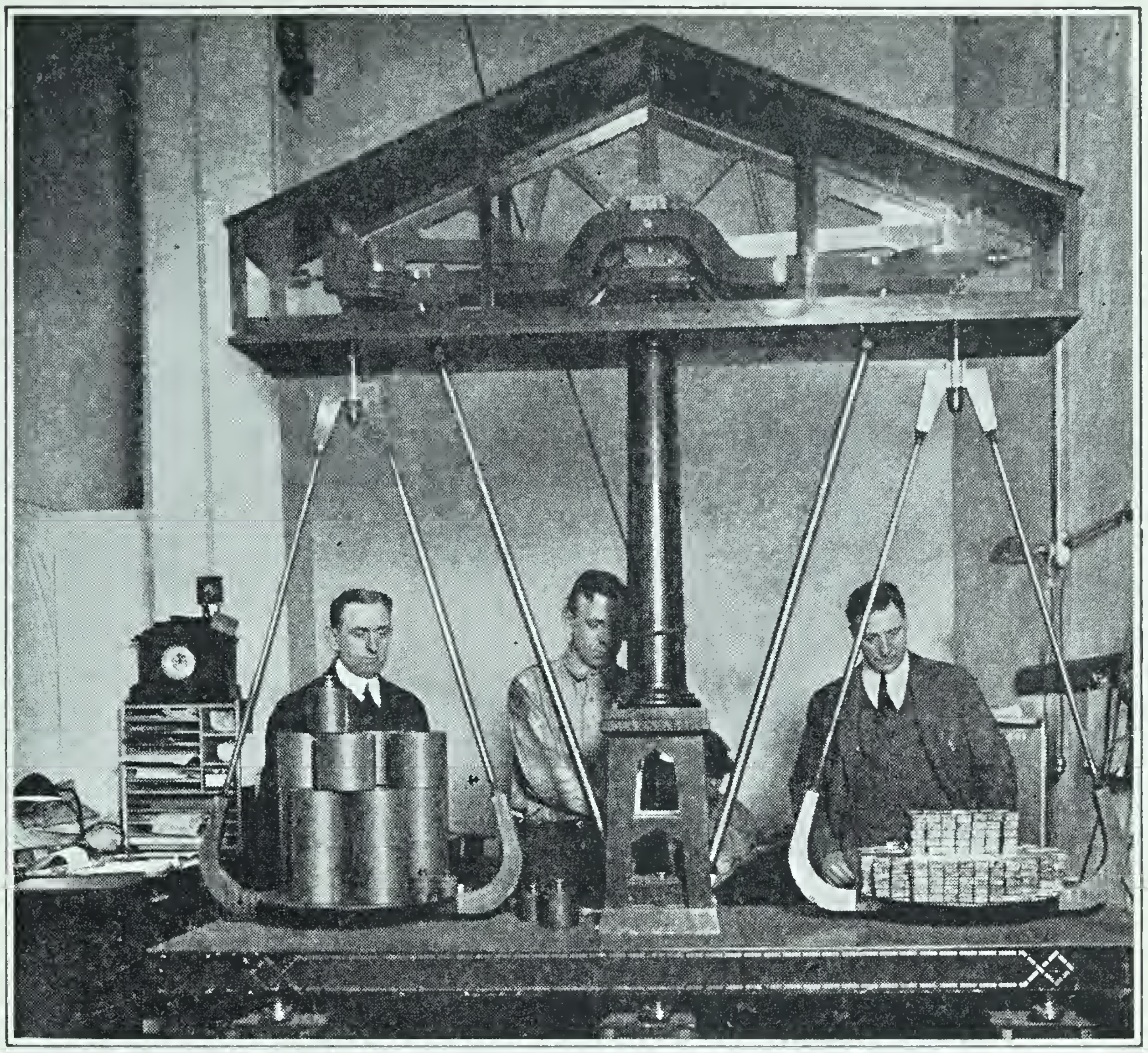
New uses give many elements new values. In this chapter we shall gather together a number of elements. Each of these has some peculiar interest, either as a pure element or for its use in alloys. We need not study the compounds of these elements except in a very brief way. Most of these elements have been known for a long time; but, with the exception of gold and platinum, their uses have been few or none. It is due to the great progress made in recent years in mechanical and chemical industry that most of them have become important.

GOLD

Some interesting properties of gold. Gold has *color*, while all other metals except copper are silvery in appearance. It is the most malleable and ductile of the metals. It can be rolled or beaten into sheets (gold foil) so thin that a pile of one hundred thousand would be only one millimeter thick. It can be drawn into wire so fine that two miles of it weigh but one troy ounce. It does not tarnish in the air, and none of the common acids acts on it. Aqua regia dissolves it, forming a compound known as *chlorauric acid* ($HAuCl_4$). Chlorine also attacks it.

The uses of gold. Gold is too soft to be used for most practical purposes; so it is always alloyed with copper or silver (sometimes with still other metals) when used for jewelry or coinage. Jewelers indicate the fineness of gold in a very old way. Pure gold is said to be 24 *carats* fine. Jewelry has long been standard at 18 carats, 18 parts being gold and 6 parts copper (red or yellow gold) or nickel or silver (white gold). Much jewelry is now 14 carats fine. Gold coinage is 90 per cent gold and 10 per cent copper.

Apart from jewelry, coinage, and dentistry, gold has few important uses. Its value is not based on its real uses but is



Keystone

Fig. 455. Weighing gold bars in one of the laboratories of the United States government

Each of the bars on the right pan of the scales has a value of about $5000. Although the scales are large, they are so delicate that even a human hair can be weighed on them

determined by arbitrary acts of governments which make gold a basis for currency (Fig. 455). It has been estimated that if all the money gold of the world were to be cast into one cube, this golden cube would weigh eighteen thousand tons and be thirty-one feet on each edge.

Where gold comes from. Many countries produce gold. Their relative production often changes as old mines are worked out and new deposits are found. South Africa is the greatest producer. Soviet Russia and Canada are large producers. In United States territory, California, Alaska, Colorado, and South Dakota lead.

Traces of gold are to be found in most soils and in sea water, that great catch basin for all sorts of compounds. It has been estimated that if the gold in all the oceans could be

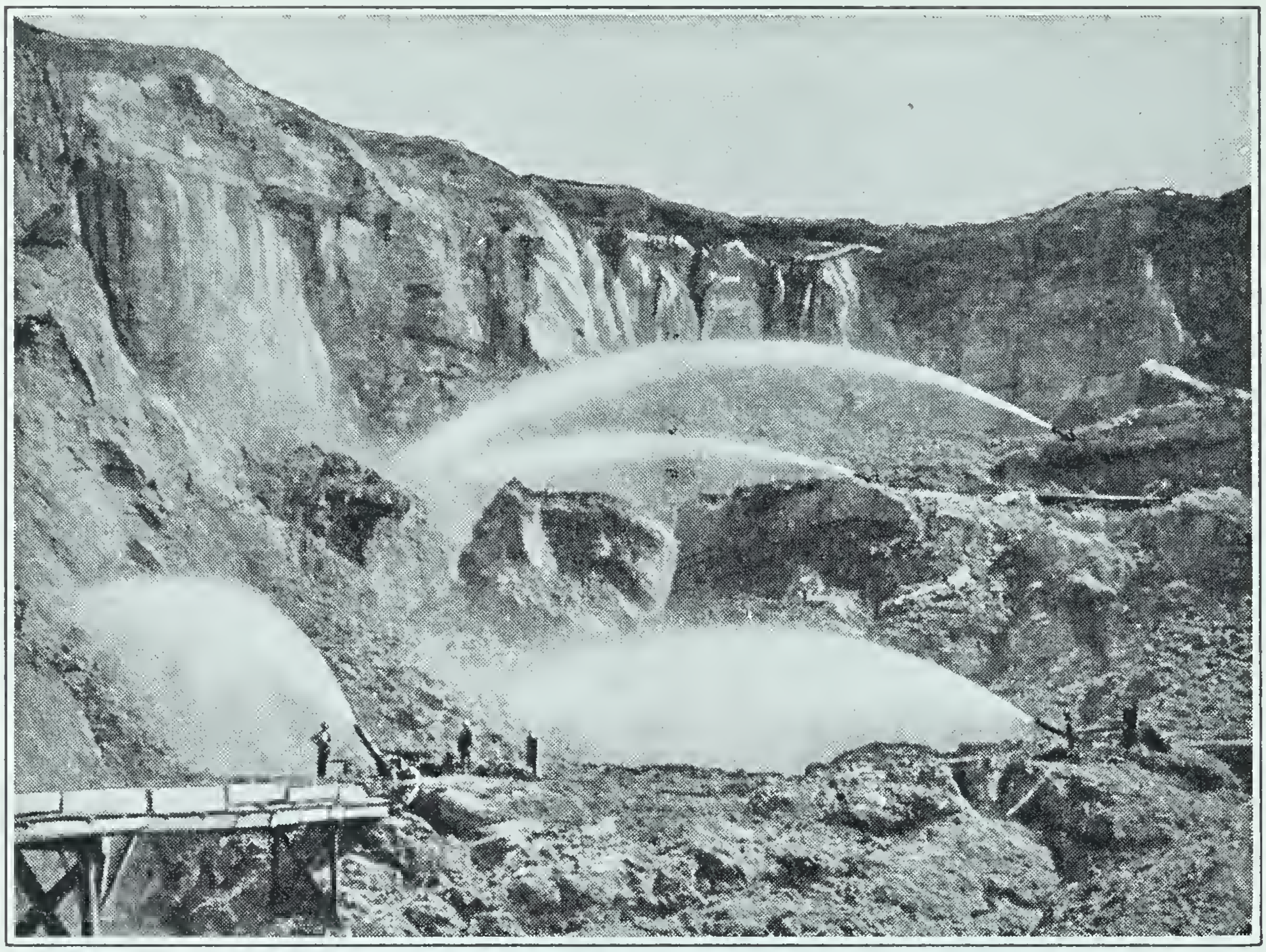


FIG. 456. The hydraulic mining of gold. The gold-bearing rocks are broken down by powerful streams of water

separated and divided equally among all the people of the United States, each person would receive approximately $25,000,000 worth of gold at present prices. But no way has been devised for getting this gold from sea waters without its costing more than it is worth.

How gold is mined. Gold occurs in large or small particles in the gravel of streams, in sand and gravel deposited long ago by streams, and in solid veins of quartz. The way of getting the gold depends on the kind of deposit being worked.

In *placer mining* the gold-bearing sand or gravel is washed in running water which carries away the lighter sand and stones and leaves the heavy gold in the basin or trough. In *hydraulic mining* the earth and sand are swept into sluices by powerful streams of water like those from a fire engine (Fig. 456).

In *quartz-mining* the quartz is stamped to powder, and the gold is then recovered in several ways. Sometimes the powder is washed over copper plates that have been coated with mercury. The gold particles stick to the mercury, and the gold is recovered by distilling off the mercury. Sometimes the powder is treated with chemicals that dissolve the gold, which is then recovered by electrolysis. A good deal of gold is got as a by-product in refining copper, silver, and lead.

PLATINUM

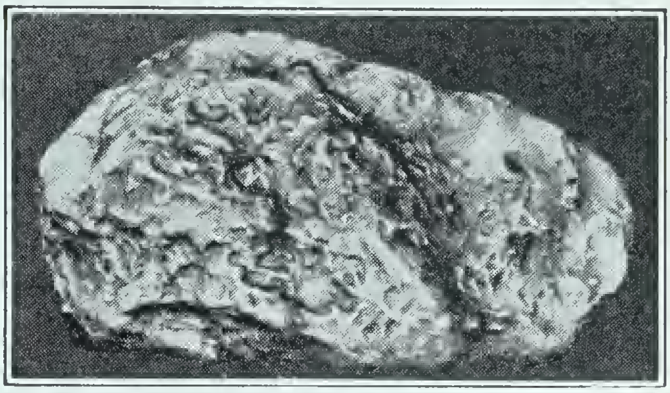


FIG. 457. The Demidoff nugget

This nugget, now in the Demidoff Museum in Leningrad, is the largest mass of platinum ever found. It weighs 7837 g (21 lb troy)

Platinum was a New World metal. The first sample of platinum came to Europe from America, in 1741; but it was the discovery of the Russian deposits, a century later, that brought the metal into real use.

Some properties of platinum. Platinum is a silver-gray metal that takes a high polish and is very malleable and ductile. It is one of the heaviest of metals (density, 21.45) and has a relatively high melting point (1755°). It is a better electrical conductor than gold.

Like gold, platinum is a very inactive element. It does not tarnish in air, and none of the common acids act on it. Aqua regia slowly dissolves it, forming *chloroplatinic acid* (H_2PtCl_6). The potassium and ammonium salts of this acid are nearly insoluble in water and in alcohol, and so the acid is an important reagent in chemical analysis.

Where platinum is found. Like gold, platinum is found in metallic grains (sometimes large nuggets (Fig. 457)), in the sand and gravel of streams, and is placer-mined. It forms a compound with arsenic, and this is apt to occur in very small quantities in the ores of copper, nickel, and similar metals. So it is a by-product in refining these metals.

The Ural Mountains, in Soviet Russia, have yielded about 90 per cent of the world's stock of platinum. The United States produces little platinum and gets most of its supply from Canada and Colombia. The placer platinum is always alloyed with other similar metals, and, as we shall see, these too have important uses.

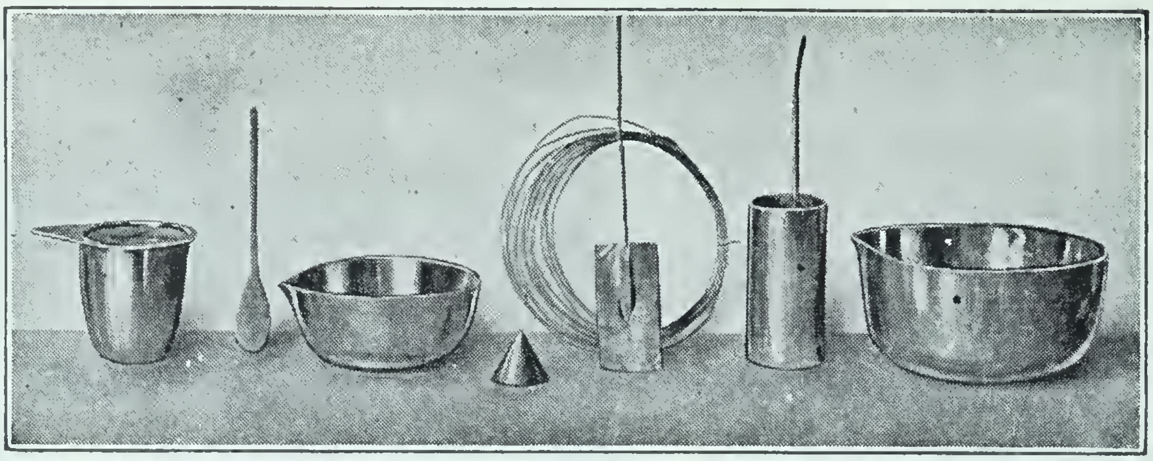


Fig. 458. Some laboratory utensils made of platinum

The uses of platinum. Platinum is more costly than gold, but its price varies greatly from month to month. It has many uses.

The chemist is chiefly interested in the many platinum appliances that must stand a high temperature or the action of strong reagents. He could not get along without the platinum crucibles, dishes, tongs, electrodes, wire, and similar things (Fig. 458) used in every laboratory. Probably more than 50 per cent of all platinum produced goes into jewelry. To a large extent it has replaced gold in popular favor. A good deal of platinum is used up in dentistry and for electrical devices, but substitutes are being developed for these uses. Another important use for platinum is as a catalyst in chemical reactions. An alloy of platinum and iridium is used for standards of weights and measures (Fig. 459).

Platinum as a catalyst. In the form of fine powder, platinum can adsorb large quantities of various gases. These gases are then in a very active condition resembling the nascent state. For example, a jet of hydrogen playing on platinum powder (in the air) at once takes fire at ordinary temperatures. A similar action takes place when sulfur dioxide and air are brought together with a platinum catalyst in making sulfuric acid (p. 363), or ammonia and oxygen in making nitric acid (p. 297).

SOME PLATINUM METALS

Five other metals, like platinum in many ways, are found alloyed with native platinum, or got as a by-product in the refining of other metals. Several of these are of interest.

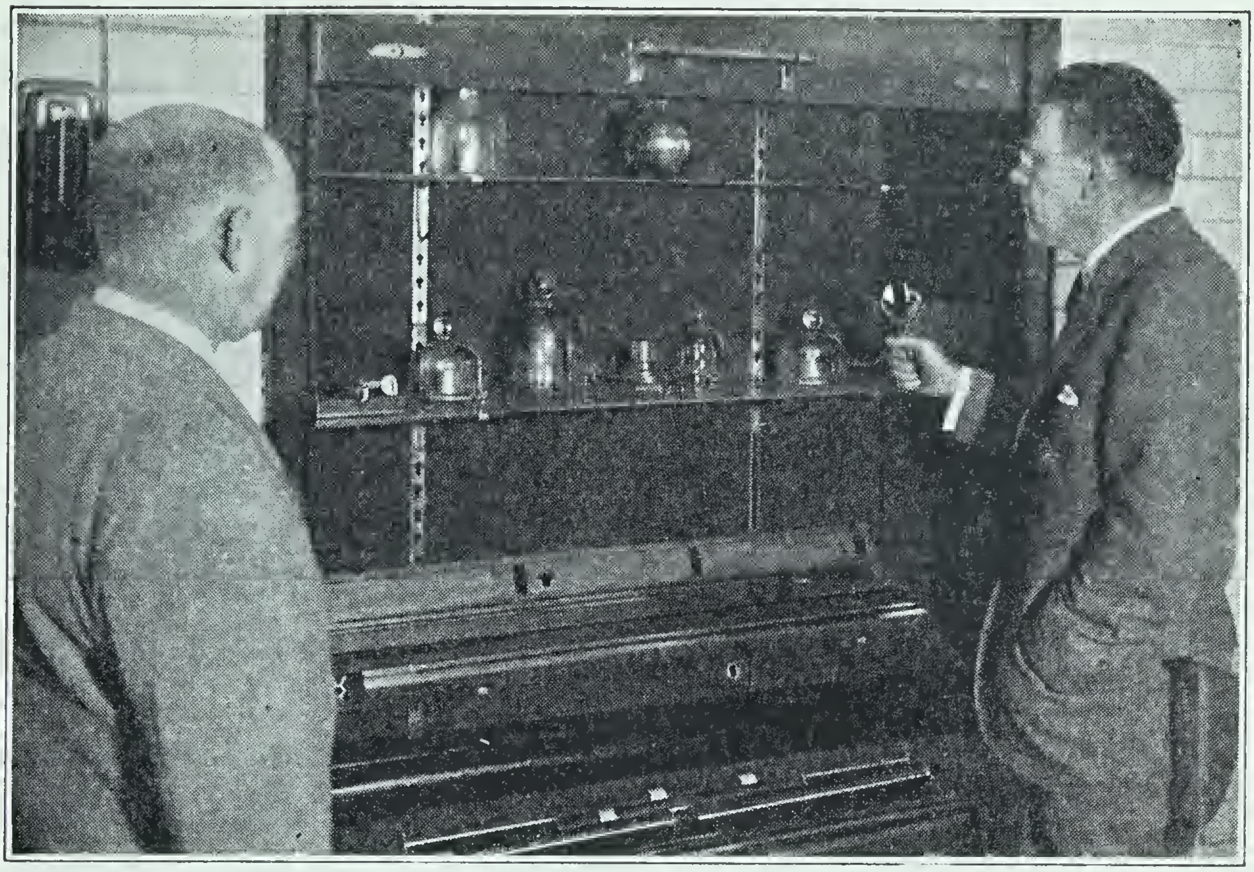


FIG. 459. Our standards of weights and measures, preserved with great care at the National Bureau of Standards, in Washington

Is the kilogram weight or the meter bar you are using accurate? To find out, they must be checked against these standards. They are made of an alloy of platinum and iridium. (Courtesy of the National Bureau of Standards)

Palladium. The most abundant of these platinum metals is palladium. It is only about half as heavy as platinum, is a little harder, but is much more easily attacked by chemical reagents. It is very useful for making scales on scientific instruments, and as a very active catalyst. It looks just like platinum, is much cheaper, and is often substituted for platinum in jewelry.

Iridium. Iridium is a hard, brittle metal and is used chiefly to alloy with platinum to harden it. These alloys are used for laboratory vessels, fountain-pen points, compass bearings, standard weights, and similar things.

SOME METALS VALUABLE IN STEEL ALLOYS

Steel's modern helpers. In the description of steel a number of metals were mentioned that are used in making alloy steels. Some of these metals have other uses, and they are all of increasing importance.

In the making of alloy steel with any of these metals, a rich iron alloy is first made by heating the oxide of the metal together with iron oxide and carbon in an electric furnace. This alloy is added in the right proportion to the liquid steel before it is poured. These alloys are given such names as *ferrovanadium* and *ferrotungsten.*

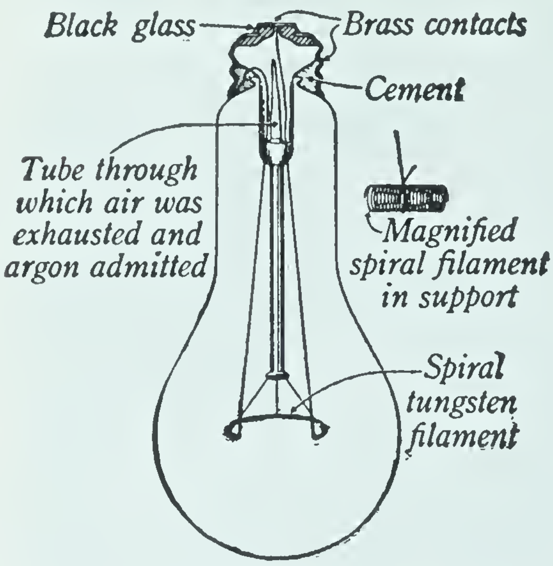

Black glass
Brass contacts
Cement
Tube through which air was exhausted and argon admitted
Magnified spiral filament in support
Spiral tungsten filament

Fig. 460. Gas-filled lamp with fine spiral filament

Vanadium. The chief commercial source of vanadium is a sulfide ore mined in the high mountains of Peru. Less concentrated ores are found in Africa and in Colorado. Vanadium steel is tough and strong and is used for many automobile parts, especially springs. Some vanadium compounds are good catalysts, used in the dye industry (for black dyes) and to replace the platinum catalyst in making sulfuric acid.

Tungsten. Tungsten ores are found in many places, China being the chief commercial source. Other large deposits are in Siam, Burma, and California. Tungsten is an important alloy metal for steels, enabling them to hold their temper at a red heat. Attention has been called to the alloy *stellite* (p. 585) and the use of tungsten carbide as a cutting tool (p. 584).

Metallic tungsten can be worked into a very malleable and ductile form, and tungsten wire is used as the filament in electric lamps (Fig. 460). Its melting point is the highest among all the metals (3370°); so the wire can be heated safely to a white heat. The metal is a good conductor; so the wire must be very fine and rather long to give the necessary resistance. Tungsten has many other electrical uses. It forms the target and the electrodes in X-ray tubes and in radio tubes, and the contact points in electrical switches, telephone jacks, automobile vibrators and distributors, and many similar devices.

Molybdenum. By far the greatest known deposit of molybdenum ore is in Colorado. The metal is very much like tungsten, but it has a lower melting point (2620°) and is not so heavy. It has come into wide use in steelmaking, molybdenum steel resembling tungsten steel in many ways. One value of molybdenum in steel seems to be that it strengthens the effect of other alloy metals and makes the steel more even in grain.

Molybdenum wire is used to support the tungsten filaments in electric lamps, and for many of the electrical purposes for which tungsten has been employed. Compounds of molybdenum are used in chemical analysis, for colored glazes, and for dyeing silk, wool, and leather.

Titanium. Titanium, in the silicon family, is an abundant element — more so than carbon or sulfur. It is found as the oxide, TiO_2, called *rutile*, as well as in many other compounds. The oxide is easily converted into *ferrotitanium*, and titanium steel is strong and resistant to wear. It is especially suited for rails at curves and terminals.

Titanium oxide is a valuable white paint pigment, in some respects better than white lead. As a rule it is mixed with other white, inert pigments, such as barium sulfate, calcium sulfate, or zinc oxide.

TANTALUM AND COLUMBIUM, NEWCOMERS AMONG THE METALS

Compounds of these two metals have been known for a hundred years, but the metals themselves have been got in pure form only in recent times. They always occur together in their ores, and are very difficult to separate and purify.

Tantalum is a metal that has many of the properties of platinum and can be used instead of platinum for many purposes. It resists chemical action of nearly every kind, except that it oxidizes at a high temperature. Next to tungsten it is the metal of highest melting point. It is especially suited for laboratory utensils, for handling corrosive liquids, and for surgical and dental tools. It takes a good edge, and can be sterilized in a flame without damage. It can be used instead of tungsten for most electrical purposes, especially for grids and shields in radio tubes.

Columbium has not been as carefully studied as **tantalum.** It looks very much like platinum and promises to be much used for jewelry, especially for watchcases. When properly heated it takes on rainbow colors that are beautiful and permanent.

CHAPTER SUMMARY IN QUESTION FORM

1. (*a*) Give three properties which gold and platinum have in common, and (*b*) state three respects in which these metals differ.

2. "The gold used for jewelry is 18 carats." (*a*) What is meant by the term *18-carat gold*? (*b*) Give two reasons why pure gold is not used for jewelry.

3. Give the composition of (*a*) a gold coin; (*b*) yellow gold; (*c*) white gold.

4. Mention three ways of extracting gold from gold deposits.

5. Tell how each of the following reagents acts upon gold: (*a*) hydrochloric acid; (*b*) sulfuric acid; (*c*) nitric acid; (*d*) aqua regia.

6. What makes platinum more expensive than gold?

7. Where are the largest known deposits of platinum located?

8. (*a*) What is a catalyst? (*b*) Why is platinum such a good one?

9. (*a*) Mention some of the uses of platinum. (*b*) Why is it used in jewelry?

10. What reagent dissolves both platinum and gold?

THOUGHT QUESTIONS

1. Platinum resembles tin, zinc, aluminum, and silver in appearance. How could you distinguish it from all these metals?

2. What action would take place if a piece of pure silver were dipped into a solution of (*a*) a gold compound? (*b*) a platinum compound? (*c*) In what process is advantage taken of this action?

3. Should a platinum crucible be used for melting lead?

4. Will nitric acid act on (*a*) pure gold? (*b*) gold coin?

OPTIONAL EXERCISES

1. Visit a jeweler and find out how he tests the purity of gold.

2. Secure samples of tungsten from burned-out electric lamps.

CHAPTER LIII

Radium and the Transmutation of Atoms

THE STORY OF RADIUM

In science one discovery leads to another. In 1895 the German physicist Roentgen discovered a new form of radiation that could pass through glass and even opaque materials like flesh, and affected a photographic plate much as light does. These were the *X rays*, by means of which the surgeon takes pictures of bones in the body (Fig. 461). This discovery started physicists everywhere on a search for new kinds of radiation.

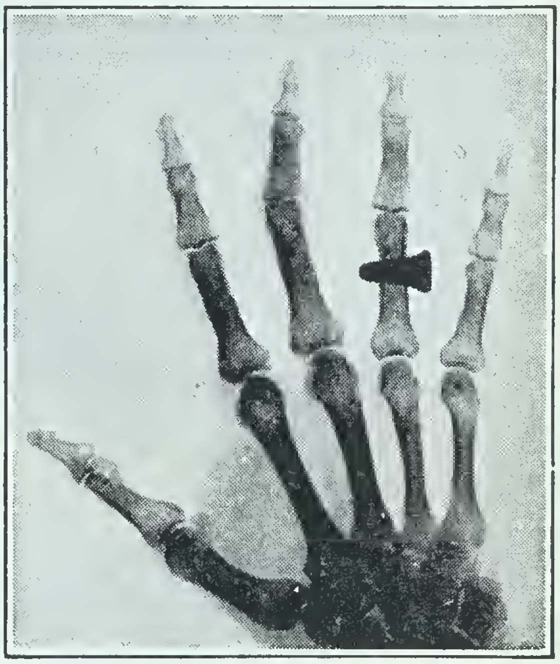


Fig. 461. An X-ray picture of a human hand

Becquerel's discovery. It had been long known that compounds of the rare element *uranium* can be seen to glow slightly in a very dark room. This led the French physicist Becquerel to see whether these compounds would affect a photographic plate protected by black paper. He found that they did, just like X rays.

He found, too, that when a charged electroscope (Fig. 464) is brought near any of these substances it loses its charge (Fig. 465), proving that the air around the uranium compounds is an electrical conductor, which ordinary air is not. This new property of uranium compounds was named *radioactivity.*

The discovery of radium. Becquerel's associates, Pierre Curie and his Polish bride, now began a thorough study of this radioactivity. They found pitchblende, the common ore of uranium (Fig. 466), to be about four times as active as the pure oxide (U_3O_8) of uranium; so radioactivity must be due to some unknown substance in the ore, rather than to

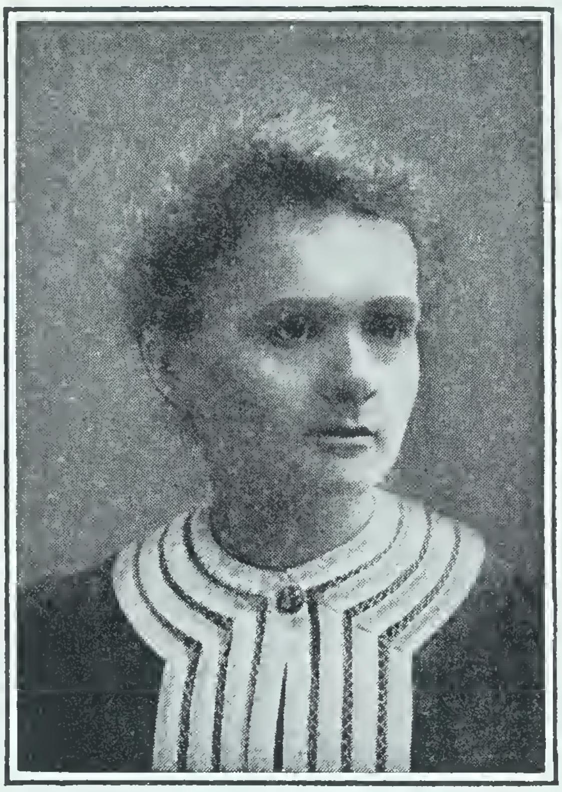


Fig. 462. Madame Marie Curie (1867–1934)

Born in Warsaw, Poland. For years professor at the Sorbonne, in Paris. Madame Curie, together with her husband, Pierre Curie, discovered polonium in July, 1898, and radium in December, 1898. Later she isolated pure radium, studied its properties, and determined its atomic weight. In 1903 the Nobel Prize was awarded to Monsieur Becquerel and Monsieur and Madame Curie conjointly, and in 1911 to Madame Curie alone. She was elected honorary member of the American Chemical Society in 1909

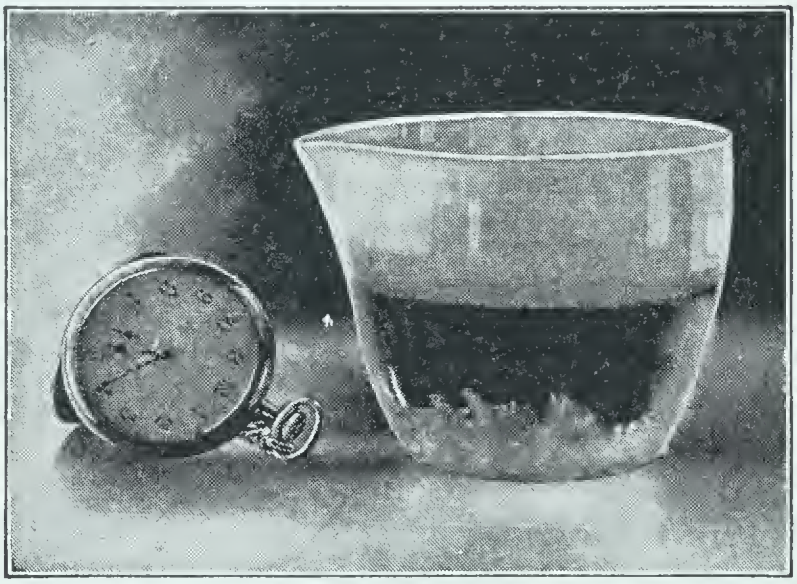


Fig. 463. Radium bromide crystallizing, and the hands of a watch made luminous by radium

A picture taken in the laboratory of the Standard Chemical Company, showing the crystallization of the radium bromide which the women of America, through the President of the United States, presented to Madame Curie on the occasion of her visit to America in 1921. A second gram of radium was presented to Madame Curie during a visit in 1929. This she dedicated to the use of her native country, Poland the uranium itself. By long-continued work on tons of the ore, in 1898 they got a minute quantity of the chloride of a new element, four million times as active as uranium oxide, and they named this element *radium.*

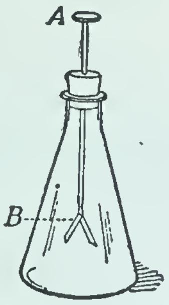


Fig. 464. A charged electroscope

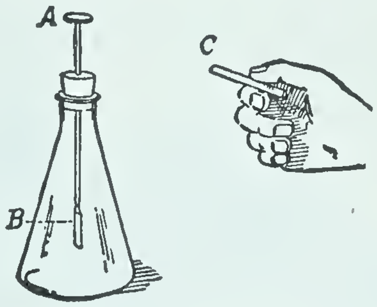


Fig. 465. A discharged electroscope

A (Fig. 464) is a metal rod to the end of which are attached two pieces of aluminum foil, *B*; when electrically charged, these repel each other. When any material containing radium is brought near the knob *A* (Fig. 465), the electroscope is discharged, and the pieces of aluminum collapse, as shown at *B*

After her husband's death by an accident, Madame Curie continued the study of radium and found its atomic weight to be 226, which placed it in the then vacant place below barium in Group II. In 1910 she isolated a minute quantity of the metal itself.

Why radium is very rare. It was soon discovered that radium is present in all uranium ores *and in no others,* and that the ratio between uranium and radium is always constant. There is always about 1 part of radium to 3,400,000 parts of uranium. Now uranium ores are themselves rare and not very rich in uranium. So it comes about that it takes approximately 15 tons of ore to produce *1 g* of radium (in the form of a salt).

The richest ores have been found near Great Bear Lake in Alberta, Canada, and in the Belgian Congo. At present Canada is able to supply all our needs, and at a reasonable cost. The finding of these richer ores has helped to lower the price to about $25,000 per gram of radium (present as a salt). The world's total production has been about 2 lb.

The radiation of radium. A salt of radium, such as the chloride, looks much like any other white salt. But if we could watch many millions of radium *atoms* in such a salt, we should here and there see one of them undergoing a violent change. As a result every compound of radium (con-

Fig. 466. Samples of pitchblende mined in Canada

Courtesy of Bureau of Mines, Ottawa

taining countless billions of atoms) keeps up a steady succession of these changes at such a rate that half of the atoms cease to be radium in 1690 years. This is called the *half-life period* of the element.

This violent change in the atom results in its giving out three kinds of so-called *rays*: alpha (α) rays, beta (β) rays, and gamma (γ) rays.

What radioactive rays are. The alpha rays have proved to be the nuclei of helium atoms (He^{++}). They are shot off from the nucleus of the radium atom with great velocity (20,000 miles per second); but they are stopped by a sheet of paper or the thinnest metal foil. The beta rays are electrons, moving with a velocity of 60,000 to 180,000 miles per second. They are more penetrating than the alpha rays, but are stopped by relatively thin sheets of metal.

The gamma rays are not moving particles; they are exceedingly short waves like X rays, but much shorter. Like X rays, they move with the velocity of light (186,000 miles per second), and are something like 100 times more penetrating than are beta rays.

Where radium comes from. Radium is decomposing steadily all the time. All compounds of radium have the same rate of change, and neither high temperature nor low temperature changes this rate. The half-life period of the

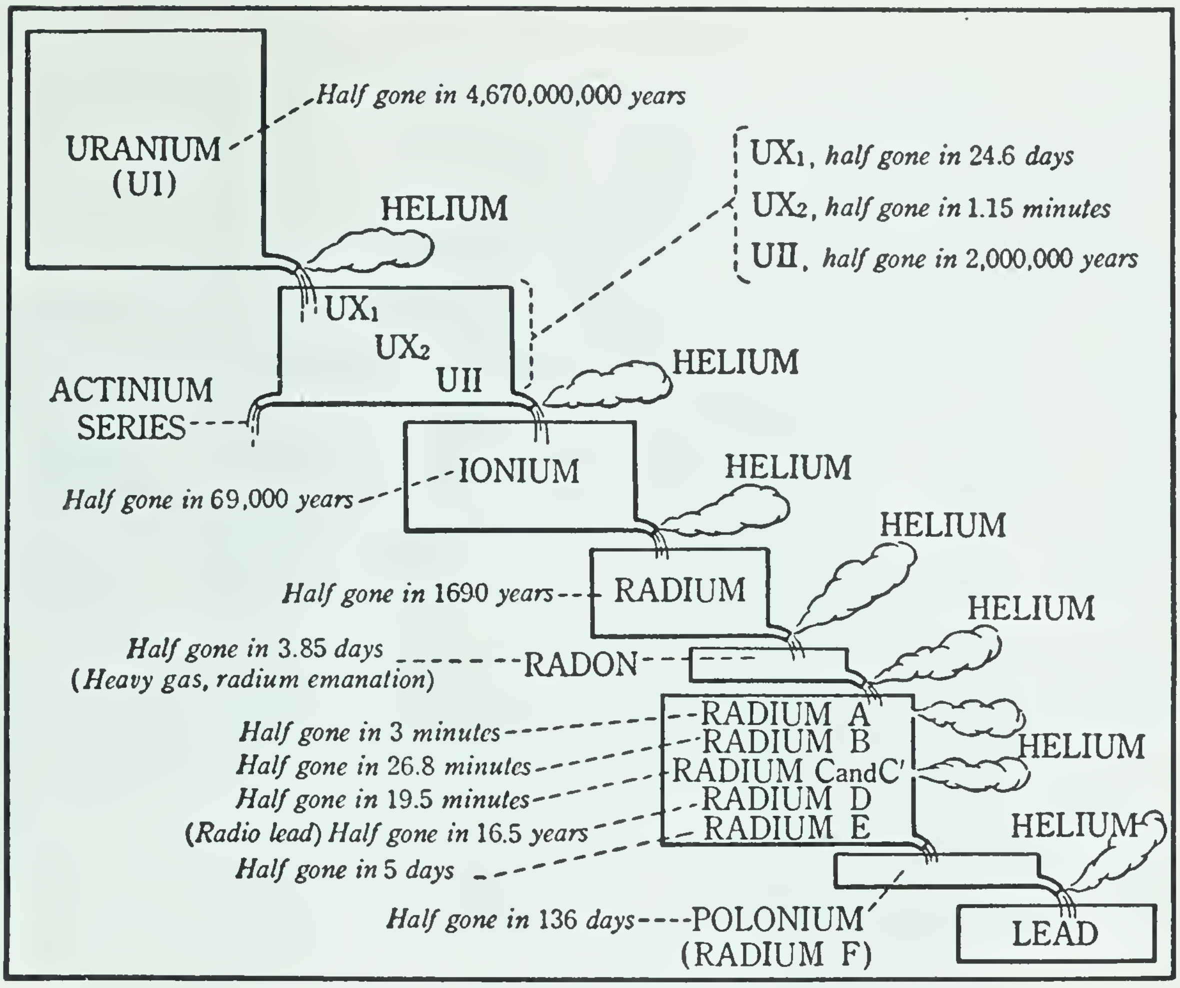

URANIUM (UI)
Half gone in 4,670,000,000 years
HELIUM
UX₁, half gone in 24.6 days
UX₂, half gone in 1.15 minutes
UII, half gone in 2,000,000 years
UX₁
UX₂
UII
ACTINIUM SERIES
HELIUM
IONIUM
Half gone in 69,000 years
HELIUM
HELIUM
Half gone in 1690 years
RADIUM
HELIUM
Half gone in 3.85 days (Heavy gas, radium emanation)
RADON
Half gone in 3 minutes
RADIUM A
Half gone in 26.8 minutes
RADIUM B
RADIUM C and C′
Half gone in 19.5 minutes
RADIUM D
(Radio lead) Half gone in 16.5 years
RADIUM E
Half gone in 5 days
HELIUM
HELIUM
Half gone in 136 days
POLONIUM (RADIUM F)
LEAD

Fig. 467. Atomic disintegration series simply illustrated

The atomic disintegration series is here illustrated by water running down through a series of tanks. The diagram shows what happens while uranium is being transmuted into lead isotope in nature. (After *Scientific American*)

element is 1690 years; yet the rocks in which it is found are hundreds of thousands of years old. Why has any radium survived?

Plainly it is being formed from some other element, and this element proves to be *uranium*. The quantity of radium in an ore of uranium is the result of a balance between its formation from uranium and its rate of going to pieces. So we shall never find a rich ore of radium.

What becomes of radium? From what has been said it might be inferred that a radium atom explodes completely into helium nuclei, electrons, and something like light (gamma rays). The real picture is not this at all but is as follows:

Beginning with uranium, a long succession of radioactive elements is produced, at least fifteen in number, related to each other in a remarkable way. When any one of these explodes, it drives out of its nucleus *either a helium nucleus* *or an electron,* and powerful short waves result. Each such explosion produces a new atom, the life of which may be long or very short. Fig. 467 represents these changes graphically.

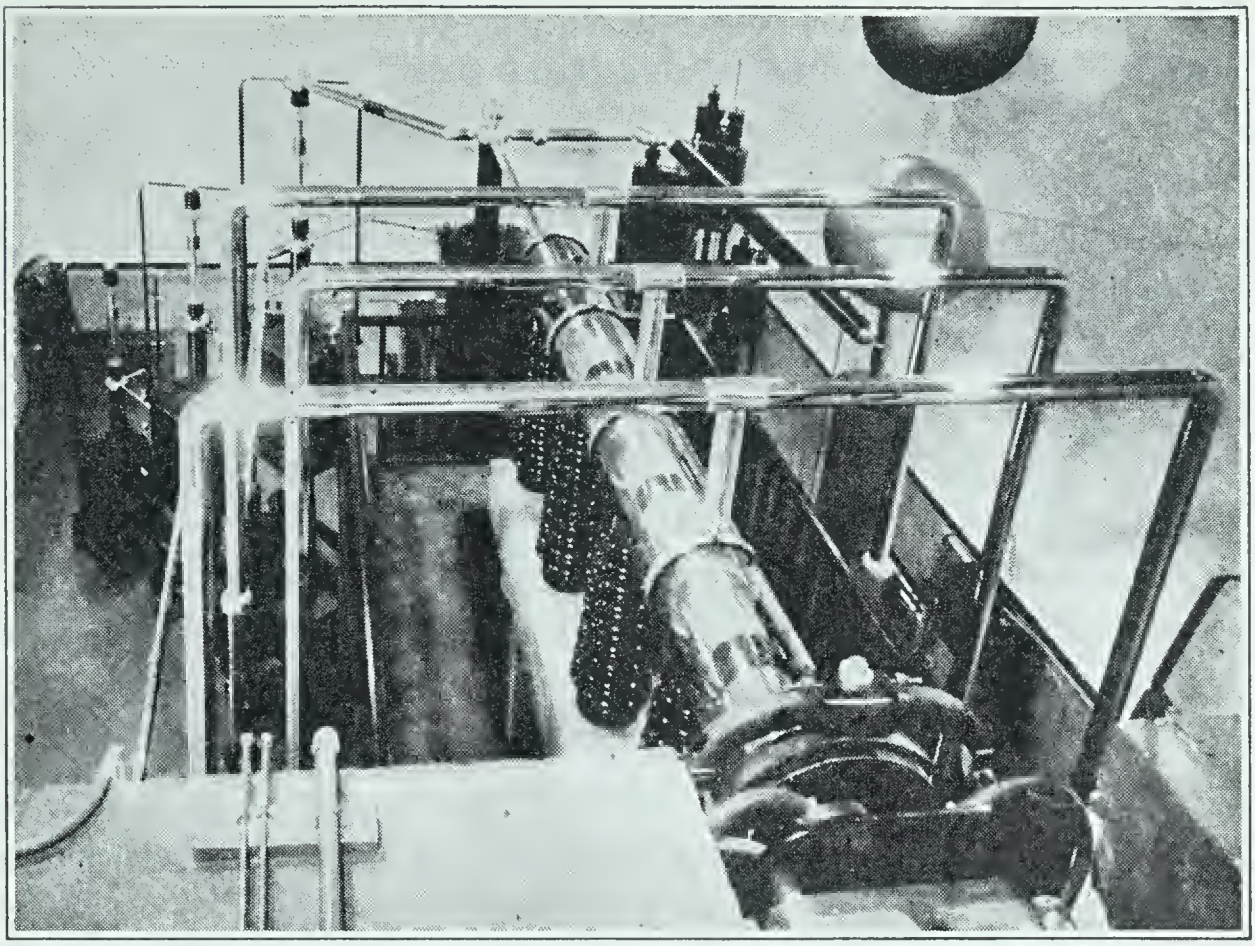
The atomic weight of uranium is 238, and that of radium 226 — a difference of 12 units. So in this interval three successive explosions have driven out three alpha rays (He^{++}) of weight 4. Each of two other explosions has driven out a beta ray (electron). This makes four new atoms *between* uranium and radium. Following radium, similar explosions occur until an end is reached in an *isotope of lead* (atomic weight 206). This explains why lead is always present in ores of uranium.

Energy of radioactivity. The energy set free in these changes is amazing, for it is much greater than that of any chemical action between atoms. The total energy set free by a gram of radium in its disintegration into lead is more than 200,000 times the heat of combustion of a gram of carbon. A sample of a radium compound is actually a little above room temperature all the time.

The importance of radium to science. The discovery of radium was a great gift to science. This strange element afforded the first definite proof that an atom is an *organization* of separate parts. In bringing the electron to our knowledge it gave us a start toward our modern views about the nature of electricity. It suggested that other atoms may possess great stores of energy and may also be radioactive. A number have been found to be so, including thorium and even potassium.

The chemical effects of radium. The radiations of radium and other radioactive elements have interesting chemical effects. They bring about decompositions in glass, water, and many other substances. Like X rays, they make bad burns on the skin and other tissues. They cause certain substances to shine in the dark, especially zinc sulfide. Enamels containing a minute quantity of radium are used to illumine the hands of watches and clocks, and the push buttons of electric lights.

The medical uses of radium. Radium kills bacteria, largely by its gamma rays. This suggested that possibly



General Electric Company

FIG. 468. A type of **X**-ray tube now coming into use in place of radium in the treatment of certain diseases

certain skin diseases, and especially cancer, might be cured by radium radiation. The idea is that the abnormal cells making up cancer tissue might be killed without injury to the normal ones. To a certain extent this treatment has been successful.

It has already been pointed out that these gamma rays are very like X rays, but are of much shorter wave length. X-ray tubes using very high voltages are now being made (Fig. 468) that give rays about as short and effective as the gamma rays from radium, and this is one great reason for the falling price of radium.

ARTIFICIAL CHANGES IN ATOMIC NUCLEI

Can we change the nucleus of an atom? It is easy to dislodge temporarily the electrons around the nucleus of an atom; but can we permanently change its nucleus? We picture the nucleus as of very small volume, intensely positive, and guarded by a far outpost of negative electrons. To change or shatter the nucleus we should have to use some sort of powerful atomic bullets that could get past the electrons and hit the small nucleus with great force. Can we think of any such bullets?

Varieties of atomic bullets. Physicists have been able to use four kinds of bullets to fire at the nuclei of atoms. These are the proton (H^+), the deuterium nucleus (D^+), the helium nucleus or alpha ray (He^{++}), and the neutron (which has no charge). The electron (beta ray) is too small in mass to do much damage, even at its great speed.

How could these bullets act? We can imagine two or three things that might happen if one of these bullets should hit the nucleus of an atom. (1) It might just knock out either a proton or a neutron. (2) It might stick in the nucleus and so increase its weight and charge. (3) It might stick, but also knock out a proton or a neutron. All these things really happen.

Chances of a hit. The chances of directly hitting a nucleus are very small. The bullets (except the neutron) are intensely positive and are fired at a still more intensely positive and very small target. The speed must be great and the aim perfect or the bullet will be pushed aside and miss the nucleus. One hit in a million tries would be wonderful marksmanship.

Results of atomic bombardment. By these bombardments the atoms of many elements have been changed into other atoms. For example, the nucleus of the lithium atom, hit by a proton (H^+), breaks down into two helium nuclei. A beryllium nucleus hit by a helium nucleus (alpha ray) becomes a carbon atom and a neutron. This is the reaction by which fast-moving neutrons are got for bombarding other atoms. An isotope of mercury even passes into a gold atom by loss of a proton.

Artificial radioactive atoms. In 1931 the daughter of Madame Curie, Irène Curie-Joliot, and her husband made the first *artificial* radioactive atoms. They bombarded aluminum with alpha rays from radium (He^{++}) and got a radioactive isotope of phosphorus, of weight 30. This radioactive phosphorus rapidly changes into an isotope of silicon, of weight 30. A very interesting achievement was the preparation of *radioactive sodium* by Lawrence, by the use of deuterium nuclei, D^+, by which means the nucleus of the sodium atom took up one neutron. This radioactive sodium (present in a salt) has a half-life of 15.5 hours and gives off very penetrating gamma rays in decomposing. It may play an important part in medicine, replacing radium.

CHAPTER SUMMARY IN QUESTION FORM

1. Name two persons whose scientific investigations paved the way for the discovery of radium by the Curies.

2. What was the nature of the discovery of each of these men?

3. Give two ways of telling whether or not an element is radioactive.

4. The Curies found that the uranium oxide ore was more radioactive than the pure uranium oxide. (*a*) What assumption did they make to explain this fact, and (*b*) to what discovery did this assumption lead?

5. Name the chief ore from which radium may be extracted.

6. (*a*) Name the so-called *rays* of radium, and (*b*) state a characteristic of each.

7. Suppose you have 1 g of radium. In about how many years will half of this be disintegrated?

8. Does there seem to be any possibility that a supply of fairly rich ore of radium will ever be found?

9. Mention the chief uses of radium.

10. Mention some of the facts of radium disintegration that help to prove the modern theory of the structure of atoms.

THOUGHT QUESTIONS

1. In addition to radium, Madame Curie discovered another radioactive element, which she named polonium. Can you suggest a reason for selecting this name?

2. A clap of thunder travels at the rate of about 1100 ft per second. Compare this speed with that of an alpha particle.

3. Does there seem to be any probability that the world's radium will ever be all disintegrated?

UNIT READINGS

Beery. *Stuff.* [Chapter XV, "Solder and Pewter," tells of tin and lead; Chapter XIII, "Cauldrons, Coins, and Cables," treats of copper; Chapter XIV, "Skillets and Skyscrapers," tells of iron; Chapter XVI, "Noble Stuff," treats of gold, silver, and platinum; Chapter XXII, "Seeing through Stuff," tells about X rays.]

Clarke. *Marvels of Modern Chemistry.* [Chapter XIX tells of iron and steel; Chapter XX discusses copper, zinc, and tin; Chapter XXI tells of some of the rarer metals.]

Curie (Eve). *Madame Curie.* [An excellent biography of Madame Curie written by her daughter Eve. Translated by Sheean.]

Foster. *The Romance of Chemistry.* [Chapter XV, "The Wonders of Radium"; Chapter XVIII, "The Marvelous Story of Iron and Steel."]

Holmes. *Out of the Test Tube.* [Read Chapter XIII, "Atom Smashing."]

Holton. "The Story of Paint and Varnish," *Journal of Chemical Education,* Vol. V, pp. 515–530, 682–696, 836–845. [Three articles, well illustrated.]

Howard. "The Story of Copper," *Journal of Chemical Education,* Vol. VI, pp. 413–431. [Interesting; many pictures.]

Jaffe. *Crucibles.* [Chapter XIII gives a good account of the life of Madame Curie.]

Neblette, Brehm, and Priest. *Elementary Photography.* [Students interested in photography will find this little book of great value.]

Ogburn. "The Platinum Metals," *Journal of Chemical Education,* Vol. V, pp. 1371–1384. [Interesting and well illustrated.]

Rohrman. "Ferrous Metals and Alloys," *Journal of Chemical Education,* Vol. XIII, pp. 55–71.

Weeks. *The Discovery of the Elements.* [Read of the discovery of the metals in which you are interested.]

The Science Leaflet. [No. 25 of recent volumes treats of tin and lead; No. 26, of iron and steel; No. 27, of nickel, cobalt, and manganese; No. 28, of the chromium family; No. 21, of the precious metals; No. 20, of radioactivity; No. 30, of the rare elements.]

The World Book Encyclopedia. [This contains excellent articles on gold, copper, and photography; simple and well illustrated.]

The Eastman Kodak Co., Rochester, N.Y., publishes a booklet entitled "How to Make Good Pictures." Inexpensive and excellent, especially for amateurs.

Note. Students interested in inks should send 10 cents to the Superintendent of Documents, Washington, D.C., for a copy of *Inks* (Circular C413 of the National Bureau of Standards). Those interested in stain removal should send 5 cents to the Superintendent of Documents, Washington, D.C., for *Stain Removal from Fabrics — Home Methods* (Farmers' Bulletin No. 1474).

APPENDIXES

A. Chemical Library

The following list contains the names of the authors and the titles of all books referred to in the Unit Readings, together with the name and address of the publisher of each and the date of publication of the latest edition.

JOURNALS

Journal of Chemical Education, Easton, Pennsylvania. The official monthly publication of the Division of Chemical Education of the American Chemical Society.

The Chemistry Leaflet, including *The Science Leaflet* (since 1942), published monthly by The Ellen H. Richards Institute at the Pennsylvania State College, State College, Pa.

BOOKS

BANCROFT. *Applied Colloid Chemistry.* McGraw-Hill Book Company, New York, 1932.

BEERY. *Stuff: the Story of Materials in the Service of Man.* D. Appleton-Century Company, New York, 1936.

BOYD. *Gasoline: What Everyone Should Know about It.* Frederick A. Stokes Company, New York, 1929.

CLARKE. *Marvels of Modern Chemistry.* Harper & Brothers, New York, 1932.

CUNNINGHAM. *Adventures in Science.* Ginn and Company, Boston, 1926.

CURIE (EVE). *Madame Curie.* Translated by Sheean. Doubleday, Doran and Company, Garden City, New York, 1937.

DARROW. *The Story of Chemistry.* Blue Ribbon Books, Inc., New York, 1930.

EGLOFF. *Earth Oil.* D. Appleton-Century Company, New York, 1933.

FABRE. *The Wonder Book of Chemistry.* D. Appleton-Century Company, New York, 1930.

FARADAY. *Chemical History of a Candle.* E. P. Dutton & Co., New York, 1933.

FINDLAY. *Chemistry in the Service of Man.* Longmans, Green & Co., New York, 1931.

FISHER. *Rubber and Its Uses.* Chemical Publishing Co., Brooklyn, New York, 1941.

FOSTER. *The Romance of Chemistry.* D. Appleton-Century Company, New York, 1936.

FRENCH. *The Drama of Chemistry.* The University Society, New York, 1937.

HARROW. *Eminent Chemists of Our Times.* D. Van Nostrand Company, New York, 1920.

HAYES. *What Makes Up the World.* Thomas S. Rockwell Company, Chicago, 1930.

HOLMES. *Out of the Test Tube.* Emerson Books, Inc., New York, 1937.

HOLMYARD. *Chemistry for Beginners.* J. M. Dent and Sons, Toronto, 1934.

HUXLEY and ANDRADE. *More Simple Science.* Harper & Brothers, New York, 1936.

JAFFE. *Chemical Calculations.* World Book Company, Yonkers, New York, 1926.

JAFFE. *Crucibles: The Story of the Great Chemists.* The World Publishing Company, Cleveland, Ohio, 1942.

KENDALL. *At Home among the Atoms.* D. Appleton-Century Company, New York, 1929.

LEONARD. *Crusaders of Chemistry.* Doubleday, Doran and Company, Garden City, New York, 1930.

Mersereau. *Materials of Industry.* McGraw-Hill Book Company, New York, 1936.
Moore and Hall. *A History of Chemistry.* McGraw-Hill Book Company, New York, 1931.
Morrison. *Man in a Chemical World.* Charles Scribner's Sons, New York, 1937.
Neblette, Brehm and Priest. *Elementary Photography.* The Macmillan Company, New York, 1937.
Noyes and Noyes. *Modern Alchemy.* Charles C. Thomas, Baltimore, Maryland, 1932.
Pigman. *A Story of Water.* D. Appleton-Century Company, New York, 1938.
Read. *Our Mineral Civilization.* The Williams and Wilkins Company, Baltimore, Maryland, 1932.
Sadtler. *Chemistry of Familiar Things.* J. B. Lippincott Company, Philadelphia, 1930.
Sherman. *Chemistry of Food and Nutrition.* The Macmillan Company, New York, 1937.
Slosson and Howe. *Creative Chemistry.* D. Appleton-Century Company, New York, 1930.
Stieglitz (and others). *Chemistry in Medicine.* The Chemical Foundation, New York, 1929.
Tilden and Glasstone. *Chemical Discovery and Invention in the Twentieth Century.* E. P. Dutton & Company, New York, 1936.
Weeks. *The Discovery of the Elements.* Journal of Chemical Education, Easton, Pennsylvania, 1935.
The World Book Encyclopedia. W. F. Quarrie and Company, Chicago.

B. Fahrenheit and Centigrade Thermometers

A thermometer is the well-known instrument used for measuring temperatures. It consists of a glass bulb joined to a thick-walled glass tube which has a very small but uniform bore and is provided with a scale marked in degrees (Fig. 469). There are two kinds of thermometers in common use: the Fahrenheit (F.), ordinarily used in our homes, and the centigrade (C.), used for all scientific purposes. These differ only in the manner in which they are graduated. In making them the bulb and a part of the tube are filled with mercury, and the bulb is then placed in melting ice. The mercury contracts until it reaches the temperature of the melting ice, and remains stationary when this temperature is reached. The height of the mercury in the tube is then marked on the tube. The thermometer is next immersed in boiling water or steam (under a pressure of 1 atmosphere). The height to which the mercury rises is again marked on the tube. In the Fahrenheit thermometer the melting point of ice is marked 32°; the boiling point of water, 212°. The space between these two points on the tube is divided into 180 equal parts (degrees). In the centigrade thermometer the two points noted above are marked 0° and 100°, respectively, and the intervening space on the thermometer

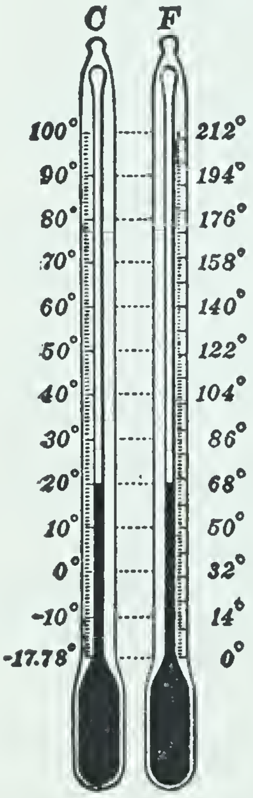


Fig. 469. Centigrade and Fahrenheit scales

tube is divided into 100 equal parts (Fig. 469). In other words, in the Fahrenheit system ice melts at 32° and water boils at 212°, while in the centigrade system ice melts at 0° and water boils at 100°. The equal divisions on the tube may be extended below the melting point of ice and above the boiling point of water.

It is easy to change readings on the Fahrenheit scale into the corresponding readings on the centigrade scale and vice versa. It is necessary only to keep in mind that 180° on the Fahrenheit scale (the difference in degrees between the melting point of ice and the boiling point of water) equals 100° on the centigrade (or 1° F. equals $\frac{5}{9}$° C.) and that 32° F. is the same as 0° C. These relations are expressed in the equation

$$\frac{C}{F - 32} = \frac{5}{9}$$

Suppose we wish to convert 75° F. into centigrade reading. Substituting 75 for F in the above equation, we have

$$\frac{C}{75 - 32} = \frac{5}{9}; \quad \text{or} \quad C = 23.8°$$

Similarly, if we wish to convert centigrade readings into Fahrenheit, we substitute the centigrade reading for C in the equation given above and solve for F.

C. *Reduction of Gas Volumes to Standard Conditions — Absolute Scale of Temperature*

In a great many chemical operations, both in the laboratory and in manufacturing plants, it is necessary to measure the volumes of gases with accuracy under various conditions. The directions in Chapter IV are not sufficient to enable one to make the necessary calculations, and a more complete explanation is here given for the guidance of those students who may become interested in this subject.

Variation of volume with pressure: Boyle's law. On page 42 Boyle's law was stated as follows: *The volume occupied by a given weight of gas varies inversely with the pressure, provided the temperature of the gas remains constant.* Thus, if a given weight of a gas occupied a volume of 1000 ml when subjected to a given pressure, it will occupy a volume of 500 ml if the pressure is doubled, or of 2000 ml if the pressure is diminished to one half. This means that for a given weight of a gas the product of the pressure and the volume will remain constant, no matter how either one may be altered. Designating the pressure and volume under one set of conditions by P and V, and under a different set by P_1 and V_1, Boyle's law may be stated thus:

$$PV = P_1V_1$$

Standard pressure. For practical purposes it is desirable to choose some *standard pressure* under which we will agree to measure all gas volumes. This is most conveniently chosen as the average pressure of the atmosphere at the sea level. This is equal to 1033 g per square centimeter. In place of expressing the pressure in this way it is much more convenient to express it in terms of the height of the column of mercury which the pressure of the atmosphere will sustain. Expressed in this way the standard pressure is equal to the pressure exerted by a column of mercury 760 mm in height, this being the average height of the barometer at the sea level.

Illustration of Boyle's law. The following example not only will make the meaning of the law clear but will also show how the law enables us to calculate the changes in the volume of a gas due to changes in pressure:

A gas measured under a pressure of 720 mm had a volume of 620 ml. What volume will this gas occupy under standard pressure, 760 mm, the temperature remaining constant?

According to Boyle's law, $PV = P_1V_1$

Substituting the values given in the problem, we have

$$760 \times V = 720 \times 620, \quad \text{or} \quad V = 587.4 \text{ ml}$$

The absolute scale of temperature. On page 43 there is a statement of Charles's law which tells us how the volume of a gas varies with the temperature measured on the centigrade scale. For many purposes it has been found more convenient to use a scale of temperature called the *absolute scale*, on which the divisions are of the same size as those on the centigrade scale, but the zero point is at − 273° on the centigrade scale; that is, the temperature at which the volume of any gas would apparently become zero (see page 43). The 0° on the centigrade scale is then 273° on the absolute scale. On such a scale all temperatures are above the zero point. To convert readings on the centigrade scale to the corresponding ones on the absolute it is necessary only to add 273°. Thus, 20° C. = 20° + 273°, or 293° A., while − 20° = − 20° + 273°, or 253° A. Fig. 470 gives a comparison of the centigrade and absolute scales at a number of temperatures.

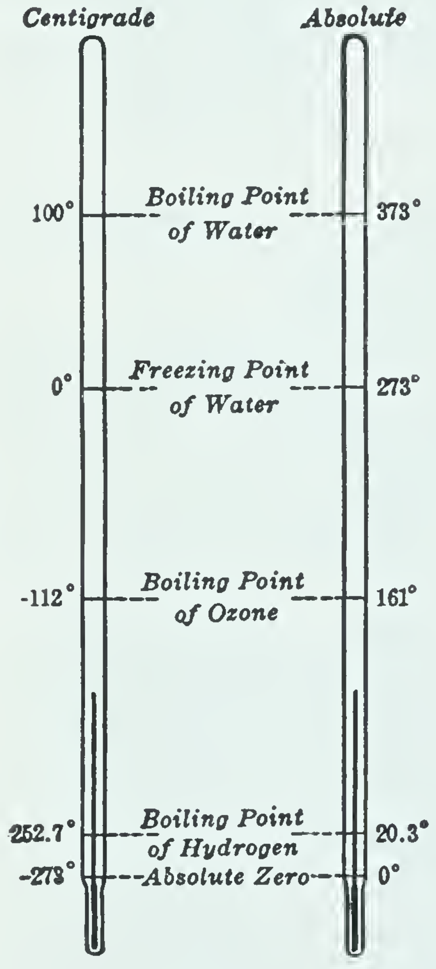


Fig. 470. Centigrade and absolute scales of temperature

Charles's law. A general statement can now be made in regard to the effect of temperature on the volume of a gas: *The volumes occupied by a given weight of a gas at different temperatures are proportional to the absolute temperatures, provided the pressure remains constant.* If V and V_1 are the volumes at the temperatures T and T_1, then $V : V_1 = T : T_1$,

or

$$V = \frac{V_1 T}{T_1}$$

This statement of Charles's law is of more general application than that given on page 43, which does not involve a knowledge of the absolute scale. The two statements, however, are equally correct.

Illustration of Charles's law. The following example will make the meaning of the law clear.

The volume of a certain gas measured at a temperature of 70° is 650 ml. What will be its volume at 10°, the pressure remaining unchanged?

First reduce the centigrade readings to absolute:

$$70°\text{ C.} = 70° + 273° = 343°\text{ A.};\quad 10°\text{ C.} = 10° + 273° = 283°\text{ A.}$$

Then substitute the appropriate values in the above equation:

$$V = \frac{650 \times 283}{343}, \quad \text{or} \quad V = 536.3 \text{ ml}$$

Variations in volume due to changes both in pressure and in temperature. In case both pressure and temperature change, then the correction may be made for each in succession, as in the following example:

A certain weight of gas measured 500 ml at a temperature of 100° when subjected to a pressure of 760 mm. Calculate the volume which this gas will occupy at a temperature of 50° and a pressure of 740 mm.

First make the correction for pressure:

$$PV = P_1V_1$$

$$740 \times V = 760 \times 500, \quad \text{or} \quad V = 513.5 \text{ ml}$$

Next make the correction for temperature:

$$V = \frac{V_1T}{T_1}, \quad \text{or} \quad V = \frac{513.5 \times 323}{373}, \quad \text{or} \quad V = 444.6 \text{ ml}$$

Vapor pressure of water. As a rule gases are measured in the laboratory by collecting them over water in a graduated tube, as represented in Fig. 471. Before the reading is taken, the tube *A* is first raised or lowered until the level of the water is the same within and without the tube; the enclosed gas is then under atmospheric pressure. But to some extent water has evaporated into the tube, and a part of the volume enclosed *is due to water vapor* and not to the gas. If the water vapor could be removed, the gas would occupy a smaller volume. The downward pressure upon the water in the tube *A* is due partly to the pressure exerted by the gas (say, oxygen) and partly to the pressure exerted by the water vapor. If we could find out how much pressure the water vapor exerts upon the surface of the water within the tube and subtract this from the atmospheric pressure, we should have the pressure which the gas itself exerts at the volume which it occupies. The pressure due to the water vapor is called the *vapor pressure of water.* It increases steadily as the temperature rises, and the table on page 642 gives its value over the usual range of temperature that occurs in the laboratory.

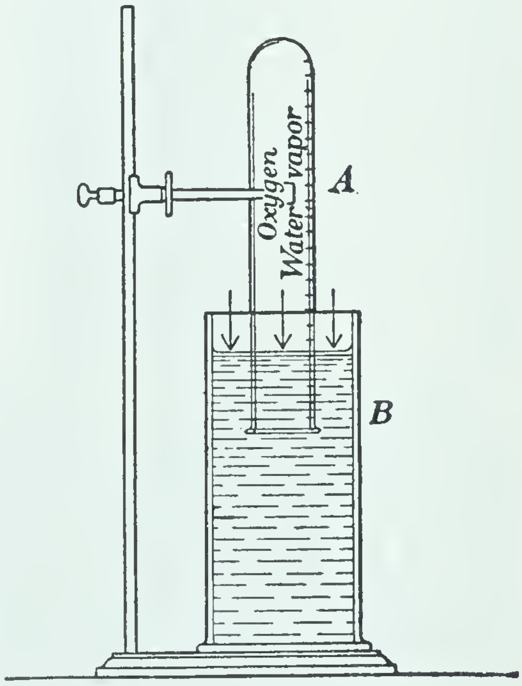


Fig. 471. Measuring the volume of a gas collected over water

Solution of problems involving calculation of volumes of gases collected over water. By referring to Fig. 471 it is evident that the atmosphere pressing down upon the surface of the water in the cylinder B tends to force the water up in the tube A and so compresses the gas in the tube. The aqueous vapor mixed with the gas within the tube tends to push the water down and thus acts in opposition to the atmospheric pressure. It is evident, therefore, that to obtain the value of the pressure to which the *gas* in the tube is subjected, we must subtract the value of the vapor pressure of water from the value of the pressure indicated by the barometer. The following example will make this clear.

A gas measured over water has a volume of 300 ml when the barometer reads 740 mm and the thermometer 20°. Calculate the volume which the gas will occupy if the pressure is increased to 760 mm, the temperature remaining constant. The effective pressure *on the gas* equals 740 mm less the vapor pressure of water at 20°, which is 17.535 mm (see table below).

$$740 - 17.535 = 722.465 \text{ mm}$$

Substituting these values in the equation expressing Boyle's law, we have

$$V \times 760 = 722.465 \times 300, \quad \text{or} \quad V = 285 \text{ ml}$$

VAPOR PRESSURE OF WATER STATED IN MILLIMETERS OF MERCURY

TEMPERATURE	PRESSURE	TEMPERATURE	PRESSURE	TEMPERATURE	PRESSURE
10°	9.209	21°	18.650	32°	35.663
11°	9.844	22°	19.827	32°	37.729
12°	10.518	23°	21.068	34°	39.898
13°	11.231	24°	22.377	35°	42.175
14°	11.987	25°	23.756	36°	44.563
15°	12.788	26°	25.209	37°	47.067
16°	13.634	27°	26.739	38°	49.692
17°	14.530	28°	28.349	39°	52.442
18°	15.477	29°	30.043	40°	55.324
19°	16.477	30°	31.824	50°	92.51
20°	17.535	31°	33.695	100°	760.00

Normal solutions. To measure the strength of a given volume of an acid or alkaline solution (such as vinegar or aqua ammonia), the chemist neutralizes the solution with what he calls a *normal solution.* A normal solution of an *acid* contains 1 gram-ion weight of H ions per liter (1.008 g). A normal solution of a *base* contains 1 gram-ion weight of OH^- ions per liter (17.008 g). From the volume of normal solution used the strength of the given solution can be calculated.

Equivalent weights. The equivalent weight of an *element* is that weight which will combine with (or displace) one gram-atom weight of hydrogen or chlorine. It is, therefore, *the atomic weight divided by the valence.* The equivalent weight of an *acid* is the weight of that acid which will yield 1.008 g of hydrogen; and the equivalent weight of a *base* is that weight of the base which will yield 17.008 g of hydroxyl.

D. *Table of Solubilities*

TABLE OF SOLUBILITIES OF SOME OF THE COMPOUNDS OF THE METALS

	Acetate	Bromide	Carbonate	Chlorate	Chloride	Chromate	Hydroxide	Iodide	Nitrate	Oxide	Phosphate	Silicate (Ortho)	Sulfate	Sulfide
Aluminum . . .	W	W		W	W		A	W	W	A	A	A	W	A
Ammonium . .	W	W	W	W	W	W	W	W	W		W		W	W
Barium	W	W	A	W	W	A	W	W	W	A	A	A	I	W
Calcium	W	W	A	W	W	X	W	W	W	X	A	A	X	X
Cobalt	W	W	A	W	W	A	A	W	W	A	A	A	W	A
Copper	W	W	A	W	W	W	A	W	W	A	A	A	W	A
Ferric	W	W		W	W	W	A	W	W	A	A	A	W	A
Ferrous	W	W	A	W	W		A	W	W	A	A	A	W	A
Lead	W	X	A	W	X	A	A	X	W	A	A	A	I	A
Magnesium . . .	W	W	A	W	W	W	A	W	W	A	A	A	W	A
Manganese . . .	W	W	A	W	W	W	A	W	W	A	A	A	W	A
Mercuric	W	W	A	W	W	X		A	W	A	A		X	I
Mercurous . . .	W	A		W	A	A		A	W	A	A		X	
Nickel	W	W	A	W	W	A	A	W	W	A	A	A	W	A
Potassium . . .	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Silver	W	I	A	W	I	A		I	W	A	A		X	A
Sodium	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Stannous	W	W			W	A	A	W		A	A		W	A
Zinc	W	W	A	W	W	W	A	W	W	A	A	A	W	A

W, soluble in water.
A, insoluble in water, soluble in either HCl or HNO_3 or in both.
I, insoluble in water and in acids.
X, slightly soluble in water and slightly or readily soluble in acids.

E. *Reference Tables, including Metric System*

DENSITIES AND MELTING POINTS OF SOME COMMON ELEMENTS

NAME	DENSITY	MELTING POINT	NAME	DENSITY	MELTING POINT
Aluminum	2.702	660°	Manganese	7.2	1260°
Antimony	6.684	630.5°	Mercury	13.546	−38.87°
Arsenic	5.7	(sublimes)	Nickel	8.9	1452°
Bismuth	9.8	271°	Phosphorus (white)	1.82	44.1°
Calcium	1.55	810°	Platinum	21.45	1755°
Carbon (diamond)	3.51	—	Potassium	0.86	62.3°
Carbon (graphite)	2.25	3500°	Radium	5 (?)	960° (?)
Chromium	7.1	1615°	Silicon	2.4	1420°
Cobalt	8.9	1480°	Silver	10.5	960.5°
Copper	8.92	1083°	Sodium	0.97	97.5°
Gold	19.3	1063°	Sulfur (rhombic)	2.07	112.8°
Iron	7.86	1535°	Tin	7.31	231.8°
Lead	11.34	327.5°	Tungsten	19.3	3370°
Magnesium	1.74	651°	Zinc	7.14	419.4°

ELECTROMOTIVE SERIES OF THE METALS

1. Lithium
2. Potassium
3. Calcium
4. Sodium
5. Magnesium
6. Aluminum
7. Manganese
8. Zinc
9. Chromium
10. Iron
11. Cadmium
12. Cobalt
13. Nickel
14. Tin
15. Lead
16. **Hydrogen**
17. Copper
18. Arsenic, antimony, bismuth
19. Mercury
20. Silver
21. Platinum
22. Gold

[For convenience this table also appears facing the inside back cover]

WEIGHT IN GRAMS OF 1 LITER OF VARIOUS GASES UNDER STANDARD CONDITIONS, AND THEIR BOILING POINTS AT 760-MILLIMETER PRESSURE

NAME	WEIGHT OF 1 LITER	BOILING POINT	NAME	WEIGHT OF 1 LITER	BOILING POINT
Acetylene	1.1621	−83.6°	Hydrogen chloride	1.6398	−85.0°
Air	1.2930		Hydrogen sulfide	1.5392	−59.6°
Ammonia	0.7708	−33.3°	Methane	0.7168	−161.4°
Argon	1.7824	−185.7°	Nitric oxide	1.3402	−151.0°
Carbon dioxide	1.9768	*	Nitrogen	1.2506	−195.8°
Carbon monoxide	1.2504	−192.0°	Nitrous oxide	1.9777	−89.5°
Chlorine	3.214	−34.6°	Oxygen	1.4290	−183.0°
Helium	0.1785	−268.9°	Sulfur dioxide	2.9266	−10.0°
Hydrogen	0.08987	−252.7°			

THE METRIC SYSTEM

Length: The unit is the *meter*, which equals 39.37 inches.
1 meter (m) = 10 decimeters (dm) = 100 centimeters (cm)
= 1000 millimeters (mm).
Volume: The unit is the *liter*, which equals 1.057 liquid quarts.
1 liter (l) = 10 deciliters (dl) = 100 centiliters (cl)
= 1000 milliliters (ml).*
Weight: The unit is the gram, which equals 15.4324 grains
= 0.03527 oz (avoir.).
1 gram (g) = 10 decigrams (dm) = 100 centigrams (cg)
= 1000 milligrams (mg).
1000 grams = 1 kilogram (kg) = 2.20462 pounds (avoir.).

RELATION BETWEEN SOME ENGLISH AND METRIC CONSTANTS

1 meter = 39.37 inches
1 liter = 1.057 liquid quarts
1 gram = 15.4324 grains
1 kilogram = 2.20462 pounds (avoir.)

1 inch = 2.54 centimeters
1 pound (avoir.) = 453.59 grams
1 ounce (avoir.) = 28.350 grams
1 U.S. gallon = 3.785 liters

1 milliliter of water at its temperature of greatest density (4°) weighs approximately 1 gram. For all ordinary purposes 1 milliliter of water may be regarded as weighing 1 gram.

F. *The Brönsted Theory of Acids and Bases*

The Brönsted theory starts with the almost certain fact that the H^+ ion (proton) does not remain a free ion in solution, but attaches itself loosely to molecules of the solvent. With water it forms the *hydronium* ion H_3O^+; with liquid ammonia, the ammonium ion NH_4^+. This well-established finding leads to ideas about acids and bases somewhat at variance with those with which we have long been familiar.

An *acid* is defined as any substance that in solution gives off protons. For example, in water the pure covalent $H:NO_3$ ionizes as represented in the equation

$$H:NO_3 + H_2O \longrightarrow H_3O^+ + NO^-_3$$

Molecules such as HCN give up very few protons to the solvent molecules and are *weak* acids. Polybasic acids, such as H_2SO_4 or H_3PO_4, give up one proton relatively easily, but the others with increasing reluctance. These ideas differ from the older ones chiefly in regard to the positive hydronium ion H_3O^+.

Conversely, a *base* is defined as any substance that in solution tends to combine with a proton more or less firmly. Water and ammonia are therefore bases, forming the ions H_3O^+, NH_4^+. In the reaction

$$H_3O^+, Cl^- + Na^+, OH^- \longrightarrow H:OH + Na^+, Cl^- + H_2O$$

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* The *milliliter* is the same as the *cubic centimeter* (cc), and both terms are used. The former is preferable and is coming into general use.

the OH^- ion acts as a *base* and the H_3O^+ ion as an *acid.* In the reaction

$$NH_4^+, Cl^- + Na^+, OH^- \longrightarrow H:OH + Na^+, Cl^- + NH_3$$

the ion OH^- is a base, and the ion NH_4^+ is an acid. In the reaction

$$Na^+, Cl^- + H_3O^+, HSO_4^- \longrightarrow H:Cl\uparrow + Na^+, HSO_4^- + H_2O$$

the ion Cl^- is a base, and the ion H_3O^+ is an acid.

In general, H_3O^+, NH_4^+, and consequently solutions of the usual hydrogen acids, are *acids*; H_2O, NH_3, OH^-, and the anions of salts (and of the usual hydrogen acids) are *bases.* In water solution the Cl^- ion has very little tendency to combine with a proton (from H_3O^+); so it is a very *weak* base. The ions CN^- and CO_3^{--} will combine with all available protons to form covalent compounds. They are very strong bases.

These ideas of acids and bases have been before chemists for a number of years. They are of especial interest and applicability in dealing with nonaqueous solutions and in biochemistry, where large molecules may give up protons in one part of their complex structure and take them up in another; that is, they may be both acids and bases at the same time. In some provinces of advanced theoretical chemistry they fit in better than does the older view, though they are not entirely free from difficulties.

It is true, however, that general chemical literature — textbooks, handbooks, dictionaries, and chemical periodicals in all languages — has not yet been recast into this newer language. Many college texts comment briefly upon the theory; but few, if any, consistently use it throughout their pages.

In aqueous solutions, the only ones with which the elementary student becomes acquainted, the advantages of the newer theory are not very pronounced. In such solutions the difference between the two systems of phraseology is a matter of definition rather than of deep significance. Until the Brönsted way of thinking is far more widely adopted in chemical literature, it seems premature to follow it in a text for secondary schools, beyond making it clear that there is this alternative system of representing the nature and the reactions of acids and bases.

SOME HELPFUL REFERENCES

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LIVINGSTON, R. J. "An Introduction to Chemical Catalysis," *Journal of Chemical Education*, Vol. 7 (1930), p. 2887. An article with many references.

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GLOSSARY

NOTE. The signs indicating the sounds of letters in the pronunciation of words are those given in Webster's International Dictionary.

Absolute temperature: temperature measured on a scale on which the zero temperature is 273° below the zero point on the centigrade scale. Centigrade readings are converted into absolute readings by adding 273° (pp. 43, 640).

Absolute zero: the zero point on the absolute scale of temperature. At this temperature all motion of the molecules ceases. It is supposed to be the lowest temperature possible.

Acid: (*a*) *Theoretical definition:* an electrovalent compound which gives positive hydrogen ions when dissolved in water (p. 258). (*b*) *Descriptive definition:* a compound whose solution in water has a sour taste, changes blue litmus to red, and reacts with bases to form salts (p. 241).

Acid, strong: an acid that gives a large percentage of active hydrogen ions when dissolved in water (p. 259).

Acid, weak: an acid that gives a small percentage of active hydrogen ions when dissolved in water (p. 259).

Alcohol: a compound derived from a hydrocarbon by replacing one or more hydrogen atoms of the hydrocarbon by an equal number of hydroxyl (OH) groups (p. 469).

Alkali (ăl'k*ȧ* lī): a strong base. The common alkalies are sodium hydroxide (NaOH), potassium hydroxide (KOH), and calcium hydroxide ($Ca(OH)_2$) (p. 242).

Allotropic (ăl ō̇ trŏp'ĭk) **forms:** forms of an element which differ from each other in chemical conduct. Example: oxygen and ozone (p. 97).

Alloy (*ă* loi'): a solid material resulting from the freezing of a melted mixture of two or more elements at least one of which is a metal (p. 506).

Amalgam (*ȧ* măl'g*ă*m): an alloy of which mercury is the principal constituent (p. 594).

Ammonia: a colorless gas whose formula is NH_3. It has a pungent odor and is very soluble in water (p. 288).

Ammonium: the name of the ion or radical NH_4 (p. 289).

Amorphous (*ȧ* môr'f*ŭ*s): the opposite of *crystalline.* A word used to describe a solid that does not crystallize (p. 50).

Analysis: the separation of a compound substance into its components (p. 124).

Anhydride (ăn hī'drīd *or* ăn hī'drĭd) **acid:** an oxide that combines with water to form an acid (p. 304).

Anhydride, basic: an oxide that combines with water to form a base (p. 304).

Anhydrous (ăn hī'dr*ŭ*s): an adjective meaning "without water." Anhydrous compounds are those that contain no water of hydration (p. 116).

Anode (ăn'ōd): the electrode connected with the positive pole of a battery (p. 74).

Aqueous (ā'kwē *ŭ*s): watery. In an aqueous solution the solvent is water.

Atmosphere: the ocean of gases surrounding the earth (p. 276).

Atom: the smallest particle of an element that exists either alone or in combination with other atoms (pp. 33, 163).

Atomic (*ă* tŏm'ĭk) **number:** the positive charge on the nucleus of an atom (p. 172).

Atomic theory: a theory that all elements are made up of atoms. Originally advanced by Dalton, and improved by others, to explain the formation of compounds (p. 166).

Atomic weight: the weight of an atom of an element compared with that of the oxygen atom, the latter being taken as 16 (p. 165).

Barometer: an instrument for measuring the pressure exerted by the atmosphere (p. 45).
Base: (*a*) *Theoretical definition:* an electrovalent compound that gives negative hydroxyl ions in aqueous solution (p. 258). (*b*) *Practical definition:* the hydroxide of a metallic element whose solution turns red litmus blue and neutralizes acids (p. 241).
Binary (bī'nȧ rĭ) **compound:** one that consists of two elements, as NaCl (p. 246).
Boiling point: the temperature at which the vapor pressure of a liquid just exceeds the opposing pressure of the atmosphere (p. 58).
Bromide (brō'mīd): a binary compound of bromine. Metallic bromides are salts of hydrobromic acid, HBr (p. 339).
By-product: a product formed along with the principal product desired in a reaction or a process (p. 229).

Calorie (kăl'ô rĭ): the unit of heat. The heat required to raise the temperature of 1 g of water 1° centigrade (p. 56).
Calorimeter (kăl ô rĭm'ê tẽr): an instrument for measuring heat (p. 55).
Carbohydrate (kär bō hī'drāt): a general name for sugars, starches, celluloses, and similar compounds. All consist solely of carbon, oxygen, and hydrogen; and, as a rule, the atoms of oxygen and hydrogen are in the ratio in which they are present in water, namely, 2 of H to 1 of O (p. 455).
Catalyst (kăt'*ȧ* lĭst): a material that by its presence changes the speed of a reaction (pp. 84, 133).
Cathode (kăth'ōd): the electrode connected with the negative pole of a battery (p. 74).
Centigrade scale: the scale of a thermometer on which the freezing point of water is 0° and its boiling point is at 100° (under standard pressure) (p. 638).
Centimeter: the one-hundredth part of a meter (p. 645).
Chemical action: the action of one substance on another that results in a chemical change (p. 190).
Chemical affinity: the force that brings about chemical action between substances (p. 29).
Chemical change: one that is due to chemical combination or decomposition (p. 12).
Chemical compound: a substance consisting of two or more elements which are chemically combined in definite proportions, and which can be represented by a formula (p. 27).
Chemical conduct: the way in which one element or compound acts with others to bring about chemical changes (p. 35).
Chemistry: the science of the composition and chemical conduct of matter (p. 14).
Chloride (klō'rīd *or* klō'rĭd): a binary compound of chlorine with some other element. Metallic chlorides are salts of HCl (p. 219).
Colloidal (k*ŏ* loi'd*ă*l) **state:** matter in exceedingly small particles distributed throughout some other kind of matter serving as a medium (p. 410).
Combustion: a chemical action in which light is given off (p. 89).
Compound: *see* Chemical compound.
Crystal: a solid that in forming has taken on a definite geometric form (p. 49).
Crystallization: the process of forming crystals.

Decomposition: the process of breaking down a compound into simpler ones or into elements, or both (p. 194).
Dehydrate: to take water from a substance, usually from a hydrate (p. 366).
Deliquescent (dĕl ĭ kwĕs'*ĕ*nt): possessing the property that some solids have of absorbing water from the air until they become moist or even pass into solution (p. 73).
Density: the weight in grams of 1 ml of a solid or liquid (p. 120); of a gas (liter-density), the weight in grams of a liter of the gas (p. 121).

Dibasic (dī bās′ĭk) **acid:** an acid that has two replaceable hydrogen atoms in its molecule (p. 243).

Disinfectant: a substance that destroys germs, especially disease germs.

Dissolve: to pass into solution in some solvent (p. 63).

Distillate (dĭs′t*ĭ* lât *or* dĭs tĭl′ât) : the liquid obtained as the product of distillation (p. 118).

Distillation: the process of converting a liquid into a vapor, and then condensing the vapor into a liquid again (p. 118).

Dry ice: solid carbon dioxide (pp. 40, 152).

Efflorescence (ĕf lô rĕs′*ĕ*ns) : the property some hydrates have of giving off water vapor when exposed to air, and crumbling into powder (p. 116).

Electricity: electricity consists of either of two fundamental units : (*a*) the electron (negative electricity) or (*b*) the proton (positive electricity). Possibly the true positive unit is the positron, and a positron combined with a neutron makes up the proton (p. 170).

Electrode (ê lĕk′trōd) : the plate attached either to the positive pole of a battery (anode) or to the negative pole (cathode) (p. 74).

Electrolysis (ê lĕk trŏl′*ĭ* sĭs) : the chemical decomposition resulting from the passage of an electric current through an electrolyte, either in solution or melted (p. 74).

Electrolyte (ê lĕk′trô līt) : a compound which in solution or when melted conducts an electric current (p. 74).

Electron: the natural unit of negative electricity (p. 170).

Electroplating: the process of depositing one metal on the surface of another metal (as cathode) by the electrolysis of a metallic electrolyte. Some nonmetals may also be deposited in the same way (p. 503).

Element: one of the 92 building materials of which all things are made (p. 26).

Emulsion: a colloidal system in which exceedingly small droplets of one liquid are dispersed throughout a second liquid, the two liquids being insoluble each in the other (p. 417).

Energy: the ability to do work. All changes in matter are due to loss or gain of energy (p. 35).

Enzyme (ĕn′zīm) : an organic catalyst formed by living cells (p. 471).

Equation, chemical: the statement of a chemical change in terms of the symbols of the elements or compounds taking part in the reaction (pp. 33, 190).

Equilibrium: a state of balance in a reaction, in which the change in one direction is just equal to the change in the other direction (pp. 96, 310).

Ester: an organic salt formed by the reaction between an organic acid and an alcohol (p. 479).

Evaporate: to cause a liquid (or solid) to pass into the state of a vapor (p. 56).

Fahrenheit (făr′*ĕ*n hīt *or* fär′*ĕ*n hīt) **scale:** the common thermometer scale on which water freezes at 32° and boils at 212° (p. 638).

Fertilizer: material added to a soil to increase its ability to produce crops (p. 381).

Filter: a device to remove a suspended solid from a liquid. In the laboratory, paper is the usual filter (p. 64).

Filtrate: the liquid from which all suspended solids have been removed by a filter (p. 64).

Filtration: the process of filtering (p. 64).

Flame: the luminous appearance that we see when one gas burns in an atmosphere of a second gas (p. 444).

Flux (flŭks) : (*a*) in soldering, a melted material that cleans the surface of a metal so solder will flow over it and stick to it (p. 396) ; (*b*) in metallurgy, a melted material that helps to bring about the liquefaction of the solids in a furnace (p. 575).

Formula: the formula of a compound is made up of the symbols of the atoms in a molecule of the compound, together with subscript figures that show the number of each kind of atoms present (pp. 33, 186).

Freezing point: the constant temperature during the change from a liquid to a solid (p. 54).

Fusion (melting): the process of changing a solid into a liquid by heating it (p. 56).

Gas: a state of matter in which the molecules are far apart, are in very rapid motion, have little attraction for each other, and tend to distribute themselves uniformly through the space that confines them (p. 46).

Gasoline: a mixture of low-boiling hydrocarbons, boiling between certain temperatures; for the most part obtained from distillation of petroleum (p. 431).

Glass: a mixture of silicates that has been fused and then allowed to cool without crystallization to form an undercooled product that is as rigid as a true solid (p. 399).

Gram: the unit of weight in the centimeter-gram system. Originally defined as the weight of 1 ml of water at 4° (p. 645).

Gram-molecular (grăm′ mô lĕk′û lẽr) **solution:** a solution containing 1 gram-molecular weight of a solute per liter of solution (p. 194).

Gram-molecular volume: the volume occupied by 1 gram-molecular weight of a pure substance. For all gases this volume (at standard conditions) is 22.4 liters (p. 181).

Gram-molecular weight: the molecular weight in grams of any pure substance (p. 193).

Haber (hä′bẽr) **process:** the process (invented by Fritz Haber) of combining nitrogen with hydrogen to form ammonia (p. 289).

Halogen (hăl′ô jĕn): any one of the members of the chlorine family (p. 334).

Heavy water: water in which one or both of the usual hydrogen atoms has been replaced by an isotope of atomic weight 2 (deuterium) (p. 331).

Hydrate: a compound, usually a salt, that has combined with a definite number of water molecules (water of hydration) (p. 116).

Hydride (hī′drīd *or* hī′drĭd): a binary compound of hydrogen with a metal.

Hydrocarbon (hī drô kär′bŏn): a binary compound of hydrogen with carbon (p. 429).

Hydrolysis (hī′drŏl′ĭ sĭs): the action of water on a salt to form a base and an acid. The reverse of neutralization (p. 522).

Hydroxide (hī drŏk′sīd *or* hī drŏk′sĭd): a compound consisting of an atom of some element, usually a metal, combined with one or more hydroxyl groups.

Hydroxyl (hī drŏk′sĭl): the univalent radical OH (p. 244).

Indicator: a compound which has one color in acid solution and a different color in a basic solution (p. 243). Some indicators are colorless in the one solution and colored in the other.

Inert (ĭn ûrt′): inactive. Having little or no tendency to react with other substances.

Infusible: incapable of being melted. Sometimes used with the meaning "very difficult to melt."

Inorganic compounds: all chemical compounds excepting those containing carbon. The original meaning was compounds that have no connection with life processes.

Ion (ī′ŏn): an electrically charged atom or radical (p. 252). An atom or radical that has gained or lost one or more of its normally present electrons.

Ionization (ī′ŏn ĭ zā′shŭn): the process of changing electrically neutral atoms or molecules into charged ions (p. 251).

Isomeric (ī′sō̇ mĕr′ĭk) **compounds:** compounds which have the same percentage composition, but different properties due to different arrangements of the constituent atoms within the molecules (p. 458).

Kerosene: a mixture of hydrocarbons obtained from petroleum and boiling between certain arbitrary limits of temperature (p. 431).

Kilogram (kĭl′ō grăm): one thousand grams (p. 645). Originally defined as the weight of a cube of water, 10 cm on an edge, measured at 4° C.

Kindling temperature: the temperature at which a slow oxidation becomes a rapid, self-supporting combustion (p. 92).

Kinetic (kĭ nĕt′ĭk) **theory:** the theory that explains many of the laws of gases and liquids on the basis of rapidly moving molecules (p. 47).

Lake: a precipitated pigment colored by adsorption of a dye (p. 559).

Law: a generalized statement of some relation existing in nature. Example: Every pure compound has a perfectly definite composition.

Liquefy: to change some other state of matter into a liquid — usually to change a gas into a liquid (p. 59).

Liquid: a state of matter in which the molecules are close together and have a considerable attraction for each other, but not enough to hold them in definite positions and form crystals. A liquid takes the shape of the containing vessel and maintains a level surface (pp. 48, 49).

Liter: the volume occupied by 1 kg of water at 4° C. Originally the volume (at 4°) of a cube of water 10 cm on each edge (p. 645).

Litmus: a vegetable indicator that is blue in alkaline solutions and red in acid solutions (pp. 227, 243).

Lubricant: a material used to diminish friction in a machine. Usually an animal, vegetable, or mineral oil (p. 431).

Lye (lī): potassium hydroxide or sodium hydroxide (p. 236).

Malleable (măl′ē̇ *ȧ* b′l): capable of being hammered or rolled into thin sheets (p. 499).

Mass: the quantity of matter in a thing (p. 120), measured by its inertia — a method independent of gravitation.

Matter: anything that has weight or occupies space (p. 24).

Melting point: the constant temperature during the change from a solid to a liquid (p. 54).

Metal: an element whose hydroxide is a base and which gives simple positive ions (pp. 304, 500).

Metallurgy (mĕt″l ûr jĭ *or* mĕ tăl′ẽr jĭ): the process of winning a metal from its ores (p. 500).

Meter: the unit of length in the metric system; it is equal to 39.37 inches (p. 645).

Micron (mī′krŏn): a very small unit of length, equal to $\frac{1}{1000}$ of a millimeter (p. 410).

Milliliter (mĭl′ĭ lē tẽr): a unit of volume equal to $\frac{1}{1000}$ of a liter. Often called a cubic centimeter (p. 645).

Millimeter: a unit of length equal to $\frac{1}{1000}$ of a meter (p. 645).

Millimicron (mĭl′ĭ mī krŏn): a unit of length equal to $\frac{1}{1000}$ of a micron (or to one millionth of a millimeter) (p. 410).

Mineral: a substance found in nature in which some especial compound (or element) is the chief constituent (p. 500).

Mixture: a material made up of two or more compounds or elements not united in chemical combination (p. 27).

Molar solutions: a solution containing one gram-molecular weight of the solute per liter of solution (p. 194).

Molecular (mô lĕk′û lẽr) **weight:** the relative weight of a molecule of a compound (or of such elements as form molecules) when compared with the weight of the oxygen molecule fixed at 32 (p. 165).
Molecule (mŏl′ê kūl) : the smallest particle of a compound when in the gaseous state (pp. 33, 163). Many elements in the gaseous state form molecules consisting of two or more atoms.
Monobasic (mŏn ō bā′sĭk) **acid:** an acid that has but one replaceable hydrogen atom in its molecule (p. 243).
Mordant: a compound, usually a metallic hydroxide, that fastens a dye on a fabric (p. 559).

Nascent (năs′*ĕ*nt) **state:** the active condition of an atom at the instant it is set free from a compound and before it has time to form molecules (p. 225).
Neutralization: (*a*) the union of an equal number of hydrogen ions of an acid and hydroxyl ions of a base to form water (p. 242); (*b*) the complete action of an acid with a base to form a salt and water (p. 258).
Neutron (nū′trŏn) : a neutral unit, of weight 1, that is a component of the nucleus of all atoms except the hydrogen atom (p. 170).
Nitrates (nī′trāts) : salts of nitric acid, HNO_3 (p. 299).
Nitrites (nī′trīts) : salts of nitrous acid, HNO_2 (p. 302).
Nonmetal: an element whose oxide is an acid anhydride, and which, either as an element or as a component of a radical, forms negative ions (p. 304).

Ore: any natural material from which a useful element or compound can be made (p. 500).
Organic chemistry: the chemistry of compounds of carbon (pp. 137, 454).
Organic compound: a compound in which carbon is a constituent element. Originally described as a compound formed in living organisms (p. 454).
Oxidation (ŏk s*ĭ* dā′sh*ŭ*n) : *Narrow definition:* combination with oxygen (p. 88). *Wider definition:* loss of one or more electrons from an atom or radical (p. 207).
Oxide (ŏk′sīd *or* ŏk′sĭd) : a binary compound of oxygen with another element (p. 89).
Oxidizing (ŏk′s*ĭ* dīz ĭng) **agent:** an agent that brings about oxidation (p. 110).
Oxyacetylene (ŏk sĭ *ȧ* sĕt′ĭ lēn) **torch:** a blowpipe which produces a flame of acetylene gas burning in oxygen (p. 436).
Oxyhydrogen (ŏk sĭ hī′drô j*ĕ*n) **blowpipe:** a blowpipe which produces a flame of hydrogen burning in oxygen (p. 110).
Ozone (ō′zōn) : an allotropic form of oxygen represented by the formula O_3 (p. 95).

Paraffin series: a name sometimes given to the methane series of hydrocarbons of the general formula C_nH_{2n+2} (p. 429).
Pasteurization (păs tẽr ĭ zā′sh*ŭ*n): the process (devised by Pasteur) of partially sterilizing foods, such as milk, by heating for a time to a temperature between 55° and 70° (p. 459).
Petroleum: a natural liquid of great complexity, from which are obtained a great variety of products, such as gasoline (p. 428).
Phlogiston (flô jĭs′tŏn) **theory:** the old theory that burning is due to the escape of a mysterious fluid called phlogiston (p. 9).
Photosynthesis (fō tō sĭn′thê sĭs) : the process taking place in plants by which sunlight causes water vapor and carbon dioxide to unite under the influence of the green matter in vegetation (chlorophyll) to form dextrose, and from it other carbohydrates (p. 466).
Physical change: a change that does not alter the chemical composition of a substance (p. 13).
Physical properties: those various qualities of a substance that can be seen or measured without altering its chemical composition (p. 35).

Pigment: the solid portion of a paint or similar product; usually a colored solid (p. 608).

Plastic: a semifluid material that can be molded or cast into a desired shape and that becomes rigid or hard on standing (like cement) or on being heated (like bakelite) (p. 422).

Polymeric (pŏl ĭ mĕr′ĭk) **compound:** a compound that exists in more than one form, the molecular weights of the more complex forms being simple multiples of that of the simplest one. N_2O_4 is a polymer of NO_2 (p. 422).

Positron (pŏz′ĭ trŏn): a unit of positive electricity equal in charge and mass to an electron, but of opposite electricity (p. 170).

Potash: the common (old) name for potassium carbonate, K_2CO_3.

Precipitate (prē sĭp′ĭ tāt): a solid formed from a solution by the interaction of two or more chemicals (p. 132) or by the coagulation of a colloidal dispersion (p. 414).

Properties: the characteristics, or qualities, of a substance (p. 35).

Proteins (prō′tē inz): complex organic compounds containing nitrogen, such as the casein of milk (p. 490).

Proton (prō′tŏn): the positive unit of electricity, with a mass of 1. Possibly a neutron associated with a positron (p. 170).

Qualitative analysis: the analysis of a substance to find out what elements are present in it.

Quantitative analysis: the analysis of a substance to find out the percentage of each of its component elements.

Quartz: a crystalline variety of silicon dioxide, SiO_2 (p. 392).

Radical: a group of atoms taking part in a reaction without change in composition (p. 244).

Rayon: a fabric manufactured from cellulose that resembles silk in appearance (pp. 463, 464).

Reaction: a chemical change. Such a change can be represented by an equation (p. 190).

Reducing agent: an agent that can bring about a chemical reduction (p. 110).

Reduction: (*a*) taking oxygen from a compound (p. 109); (*b*) causing an element or a radical to gain one or more electrons (p. 207).

Reversible reaction: a reaction that can go in either direction, depending on the surrounding conditions of temperature, pressure, and concentration (p. 309).

Salt: (*a*) a compound formed by replacing one or more atoms of hydrogen of an acid by atoms of a metal (p. 242); (*b*) a compound formed from the cations of a base and the anions of an acid (p. 259).

Salt, acid: (*a*) a compound formed by replacing only a part of the hydrogen atoms of an acid by atoms of a metal (p. 243); (*b*) a compound formed from hydrogen ions, metal ions, and bivalent or trivalent anions.

Salt, basic: (*a*) a compound formed by replacing only a part of the hydroxyl group of a base having more than one hydroxyl group by an acid radical (p. 243); (*b*) a compound made up of a polyvalent metallic ion, a basic hydroxyl ion, and an acid anion. Example, $Pb(OH)(NO_3)$ (p. 243).

Salt, normal: (*a*) a compound formed by replacing all the hydrogen of an acid by metallic atoms (p. 243); (*b*) a compound formed from metallic cations and acid anions (p. 259).

Science: knowledge organized in such a way as to be of service in gaining further knowledge (p. 20).

Solid: a substance that retains its shape unless subjected to great pressure (p. 49).

Solubility: the quantity of a given substance that will saturate a stated quantity of a given solvent (usually a liquid) at a given temperature (p. 66). The quantity of both solute and solvent may be stated in several ways (p. 71).

Solute (sŏl′ūt): the substance dissolved in a solvent to make a solution (p. 63).

Solution: a substance (usually a liquid) in which a second substance (solute) has been dissolved (p. 63).

Specific gravity: the ratio between the weight of a given volume of a substance and that of an equal volume of some liquid (water) chosen for comparison, both measured at the same temperature, usually 18° (p. 121).

Spectroscope (spĕk′trô skōp): an instrument for analyzing light into its component wave lengths (pp. 272, 273).

Spectrum: the pattern of colored lines from a source of light as shown by the spectroscope (p. 273).

Spontaneous combustion: combustion which originates in a slow reaction (oxidation) that grows faster of itself until the kindling temperature is reached, resulting in rapid combustion (p. 92).

Stable compound: one not easily decomposed by heat (p. 115).

Standard conditions: conditions of temperature (0°) and of pressure (760 mm) chosen as standard for measuring gas volume (p. 44).

Substance: a general term for any definite material, whether element, compound, or mixture (p. 28).

Sugar: a group of carbohydrates. Ordinary cane or beet sugar is sucrose, $C_{12}H_{22}O_{11}$ (p. 455).

Sulfates: salts of sulfuric acid, H_2SO_4 (pp. 366, 367).

Sulfides: (*a*) binary compounds of sulfur with a metal (p. 352); (*b*) salts of hydrosulfuric acid, H_2S (hydrogen sulfide) (p. 355).

Sulfites: salts of sulfurous acid, H_2SO_3 (p. 361).

Supersaturated solution: a solution that contains more of the solute than could be dissolved in the presence of excess solid solute (pp. 66, 67).

Suspension: very finely divided solid stirred evenly through a liquid and slow in settling by gravity (p. 64).

Symbol: the letter or letters used to designate an element (p. 32).

Synthesis (sĭn′thê sĭs): the formation of a compound by putting together the elements of which it is composed (p. 124).

Temperature: the intensity of heat in a given body as measured by a thermometer (p. 55).

Tempered: a metal is tempered when enough of its natural brittleness has been removed (by reheating) to adapt it to some special use (p. 579).

Ternary (tûr′nȧ rĭ) **compound:** one that is composed of three different elements; for example, $KClO_3$ and H_2SO_4.

Theory: a likely guess or mental picture formed in the effort to explain some regularity or relationship in nature (pp. 46, 47).

Transmutation: the changing of one element into another by some laboratory process; especially the changing of a base metal into gold (p. 6 and Chapter LIII).

Ultraviolet light: those waves of light that lie above (are shorter than) the shortest violet lines of the spectrum (Fig. 194).

Valence (vā′lĕns): (*a*) the valence of an atom is the number of hydrogen atoms it can hold in combination or displace from a compound (p. 198); (*b*) the valence of an atom is the number of electrons it can lose or gain or can share in pairs with another atom (p. 205).

Valence electrons: those electrons in the outer incomplete orbit of an atom that it can lose or gain or can share in pairs with another atom (p. 205).

Vitamins (vī′tȧ mĭnz): a group of complex organic compounds, components of many foods, and necessary for their digestion and assimilation (p. 490).

Volatile (vŏl′ȧ tĭl): easily converted into a vapor.

Vulcanized rubber: crude rubber that has been mixed with sulfur and heated (p. 421).

Water, hard: water containing metallic ions that form insoluble compounds with soap (p. 565).

Water, heavy: water in which one or both of the usual hydrogen atoms has been replaced by an isotope of atomic weight 2 (deuterium) (p. 331).

Water, permanently hard: water that remains hard after boiling (p. 565).

Water, soft: water that forms no insoluble compound with soap (p. 566).

Water, temporarily hard: a hard water that is rendered soft by boiling (p. 565).

Water, vapor pressure of: the pressure exerted on the walls of a confining vessel by the escaping vapor of water at a given temperature (p. 58).

Water of crystallization: the same as water of hydration (p. 116).

Water of hydration: water taken up in definite molecular ratios by many compounds as they crystallize from water. Example, $CuSO_4 \cdot 5\,H_2O$ (p. 116).

X rays: exceedingly short waves (resembling those of light) given off from an excited vacuum tube when high-speed electrons strike a metal target in the tube (p. 627).

Zeolite (zē′ō̇ līt) **process:** a process in which the metal ions of a hard water take the place of sodium ions in a complex silicate (a zeolite) as the hard water flows through a filter of the silicate (p. 567).

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ELEMENTS IN MORE COMMON USE

Their Symbols, Approximate Atomic Weights, and Usual Valences

ELEMENT	SYMBOL	APPROX. AT. WT.	VALENCES	ELEMENT	SYMBOL	APPROX. AT. WT.	VALENCES
Aluminum	Al	27	+ 3	Iron . . .	Fe	56	+ 2, + 3
Antimony	Sb	122	+ 3, + 5	Lead . .	Pb	207	+ 2
Argon . .	A	40	0	Magnesium	Mg	24	+ 2
Arsenic .	As	75	+ 3, + 5, − 3	Mercury .	Hg	200.5	+ 1, + 2
Barium .	Ba	137	+ 2	Nickel . .	Ni	58.7	+ 2
Bismuth .	Bi	209	+ 3	Nitrogen .	N	14	− 3, + 3, + 5
Bromine .	Br	80	− 1	Oxygen .	O	16	− 2
Calcium .	Ca	40	+ 2	Phosphorus	P	31	− 3, + 3, + 5
Carbon .	C	12	+ 4, − 4	Potassium	K	39	+ 1
Chlorine .	Cl	35.5	− 1	Silicon . .	Si	28	+ 4
Cobalt . .	Co	59	+ 2	Silver . .	Ag	108	+ 1
Copper .	Cu	63.6	+ 1, + 2	Sodium .	Na	23	+ 1
Gold . .	Au	197	+ 1, + 3	Sulfur . .	S	32	− 2, + 6
Hydrogen.	H	1	+ 1	Tin . . .	Sn	119	+ 2, + 4
Iodine . .	I	127	− 1	Zinc . . .	Zn	65	+ 2

RELATION BETWEEN SOME ENGLISH AND METRIC CONSTANTS

1 meter = 39.37 inches
1 liter = 1.057 liquid quarts
1 gram = 15.4324 grains
1 kilogram = 2.20462 pounds (avoir.)
1 inch = 2.54 centimeters
1 pound (avoir.) = 453.59 grams
1 ounce (avoir.) = 28.350 grams
1 U.S. gallon = 3.785 liters

1 milliliter of water at its temperature of greatest density (4°) weighs approximately 1 gram. For all ordinary purposes 1 milliliter of water may be regarded as weighing 1 gram.

WEIGHT IN GRAMS OF 1 LITER OF VARIOUS GASES UNDER STANDARD CONDITIONS, AND THEIR BOILING POINTS AT 760-MILLIMETER PRESSURE

NAME	WEIGHT OF 1 LITER	BOILING POINT	NAME	WEIGHT OF 1 LITER	BOILING POINT
Acetylene	1.1621	− 83.6°	Hydrogen chloride	1.6398	− 85.0°
Air	1.2930	*	Hydrogen sulfide .	1.5392	− 59.6°
Ammonia	0.7708	− 33.3°	Methane	0.7168	− 161.4°
Argon	1.7824	− 185.7°	Nitric oxide . . .	1.3402	− 151.0°
Carbon dioxide . .	1.9768	†	Nitrogen	1.2506	− 195.8°
Carbon monoxide .	1.2504	− 192.0°	Nitrous oxide . .	1.9777	− 89.5°
Chlorine	3.214	− 34.6°	Oxygen	1.4290	− 183.0°
Helium	0.1785	− 268.9°	Sulfur dioxide . .	2.9266	− 10.0°
Hydrogen . . .	0.08987	− 252.7°			

* Air is a mixture and hence has no constant boiling point.

† Under a pressure of 1 atmosphere, carbon dioxide vaporizes without melting. Under a pressure 5.2 atmospheres it melts at − 56.6°.

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TABLE OF THE CHEMICAL ELEMENTS, INCLUDING THEIR SYMBOLS, THEIR ATOMIC NUMBERS, AND THEIR ATOMIC WEIGHTS

NAME	SYMBOL	ATOMIC NUMBER	ATOMIC WEIGHT	NAME	SYMBOL	ATOMIC NUMBER	ATOMIC WEIGHT
Aluminum	Al	13	26.97	Molybdenum	Mo	42	95.95
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.2
Bismuth	Bi	83	209.00	Oxygen	O	8	16.000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	30.98
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.096
Carbon	C	6	12.010	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Protoactinium	Pa	91	231.
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222.
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium	Cb	41	92.91	Rubidium	Rb	37	85.48
Copper	Cu	29	63.57	Ruthenium	Ru	44	101.7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150.43
Erbium	Er	68	167.2	Scandium	Sc	21	45.10
Europium	Eu	63	152.0	Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.06
Gadolinium	Gd	64	156.9	Silver	Ag	47	107.880
Gallium	Ga	31	69.72	Sodium	Na	11	22.997
Germanium	Ge	32	72.60	Strontium	Sr	38	87.63
Gold	Au	79	197.2	Sulfur	S	16	32.06
Hafnium	Hf	72	178.6	Tantalum	Ta	73	180.88
Helium	He	2	4.003	Tellurium	Te	52	127.61
Holmium	Ho	67	163.5	Terbium	Tb	65	159.2
Hydrogen	H	1	1.0080	Thallium	Tl	81	204.39
Illinium	Il	61	?	Thorium	Th	90	232.12
Indium	In	49	114.76	Thulium	Tm	69	169.4
Iodine	I	53	126.92	Tin	Sn	50	118.70
Iridium	Ir	77	193.1	Titanium	Ti	22	47.90
Iron	Fe	26	55.85	Tungsten	W	74	183.92
Krypton	Kr	36	83.7	Uranium	U	92	238.07
Lanthanum	La	57	138.92	Vanadium	V	23	50.95
Lead	Pb	82	207.21	Xenon	Xe	54	131.3
Lithium	Li	3	6.940	Ytterbium	Yb	70	173.04
Lutecium	Lu	71	174.99	Yttrium	Y	39	88.92
Magnesium	Mg	12	24.32	Zinc	Zn	30	65.38
Manganese	Mn	25	54.93	Zirconium	Zr	40	91.22
Mercury	Hg	80	200.61				

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